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COAL CHARACTERIZATION GROUP.

DEPARTMENT OF CHEMISTRY. St Francis Xavier University.

FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY (FTIR-PAS) AS AN ANALYTICAL TOOL FOR EVALUATION OF THE EFFECTS OF WEATHERING AND/OR OXIDATION ON THE COMBUSTION BEHAVIOR OF BITUMINOUS COALS - PHASE I

FINAL REPORT

By

Brian M. Lynch and Lai-Im Lancaster

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ABSTRACT

Photoacoustic Infrared Fourier Transform (P A I F T) Spectroscopy has been used to explore the organic and inorganic structural features in a series of samples of variously treated bituminous and sub-bituminous coals, and of fractionated portions of the bulk coals. Approximately two hundred distinct samples were examined derived from or related to those provided.

The report is a selective and partial summary of portion of the available results, with emphasis on the analytical potential of PAIFT methods, since the massive information content of the data base itself, and possible substractive and corrective procedures applicable to the spectra, make it impractical to include and discuss the complete matrix of results.

Primary attention was focused on the following experimental and interpretive aspects:

1. OXIDATION

Assessments were made of the extent of oxidation of artificially oxidized coals provided by CANMET, and of sequences of artificially oxidized coals treated at St. Francis Xavier University.

Three appropriate techniques have been developed to indicate the extent of oxidation in these coal samples:

evaluation of the increasing high-frequency asymmetry of the 1600 cm.-1 band by (i) peak half-width, or by (ii) half-peak integrated intensity, or (iii) chemical derivatization by quantitative methylation, prbviding "chemical deconvolution" of the various carbonyl-type functionalities.

2. OXYGEN DISTRIBUTION IN SEMICOKES

A series of semicokes formed at 400 and at 550 degrees Celsius derived from fresh and oxidized bituminous coals were examined directly and after chemical derivatization. There are considerable differences in oxygen functionality distribution for the lower-temperature semicokes derived from the oxidized versus the fresh coals, but the higher-temperature semicokes show little difference.

3. CHEMICAL AND "SOFTWARE-CONTROLLED" DEMINERALIZATION

Fractions of the mineral-rich "sink" fractions were demineralized by chemical treatment with strong acids, and subtractive spectra were used to indicate the types of mineral-matter responsible for absorptions extraneous to the organic matrix of the coal. It was found possible to simulate the PAIFT spectra of chemically demineralized coals by computer-controlled subtraction of the mineral-matter spectrum from that of the as-received coal.

4. MISCELLANEOUS PAIFT SPECTRA OF OTHER SUPPLIED COALS

Aspects of the variations in and among spectra of other samples of bituminous and sub-bituminous coals are presented and discussed. The scope of subtractive procedures in revealing and enhancing developing or disappearing structural features is also illustrated.

PROTOCOLS FOR SAMPLE PREPARATION

All samples for PAIFT measurements were dried at 100 degrees Celsius in a Fisher Vacuum Oven for at least 3 h before examination. Dried samples were stored in sealed vials in desiccators. Samples were packed to constant pressure using a packing device based upon a screw micrometer.

PAIFT SPECTRA

The spectra were acquired using a Bruker IFS110 purge Spectrometer interfaced with a Princeton Applied Research Model 6003/6005 Photoacoustic Spectrometer.

Interferograms were obtained over a spectral range from 4,000 to 400 cm-1 using 128 scans at a nominal resolution of 8 cm-1 with a zero-filling factor of 2, Fourier-transformed and ratioed against the photoacoustic response of a vacuum-dried sample of Fisher C-198 Lampblack Carbon, to provide photoacoustic infrared spectra with encoding at intervals of 4 cm-1.

The interferometer mirror velocity setting was 2, corresponding to a mirror velocity of 0.08333 cm sec-1, and an optical velocity of 0.33333 cm sec-1.

For plotting, the ratioed spectra were smoothed using the computer's smoothing function setting of 4, which uses an eleven-point moving average to weight individual data points.

The spectral files are stored permanently on Memorex hard disks in the unsmoothed mode.

TYPICAL FEATURES OF P A I F T SPECTRA OF COALS

The major features of the infrared spectra of coals which we have found to be of use in structural diagnosis and elucidation are:

(i) O-H stretch region, 3600-2800 cm.-1

(ii) C-H stretch (a) aromatic, 3100-3000 cm.-1

(b) aliphatic, 3000-2800 cm.-1, embodying antisymmetric (3000-2900 cm.-1) and symmetric (2900-2800 cm.-1) stretching modes.

(iii) "1600 cm.-1" band, resulting from C-C multiple bond (aromatic) stretching with intensity enhanced by ring hydroxyl groups.

(iv) aliphatic C-H scissoring deformation around 1450 cm.-1.

(v) aromatic C-H out-of-plane deformation as a characteristic triplet between 950 and 700 cm.-1.

In addition, oxidized coals exhibit absorption around 1720-1650 cm.-1 resulting from various types of carbonyl functionality. We have shown in earlier reports that the individual types of carbonyl functionality present in an oxidized coal may be resolved through the device of quantitative methylation of the acidic functional groups within the coal. Thus the following types of carbonyl functionality are suggested as being responsible for discrete bands in the following regions:

1650 cm.-1 : anthrone, phenanthrone, or benzophenone

1700, 1680 cm.-1: aryl alkyl ketone and methoxyaryl alkyl ketone

1720 cm.-1 methoxycarbonyl groups attached to aromatic rings

1735 cm.-1 ortho-sited pairs of methoxycarbonyl groups attached to aromatic rings.

Other bands assignable to the mineral-matter components of coal are detectable in many Western Canadian coals. Thus, absorptions around 800, 1050, and 3650 cm.-1 are assigned to Si-O vibrations and with O-H stretching in hydrated aluminosilicate materials.

TABLE 1

LISTING OF COAL SAMPLES SUPPLIED BY ENERGY RESEARCH LABORATORIES

#	E R L #	Sample description
1.	P-303	Devco bituminous coal, Fresh (Phalen seam)
2.		Oxidized 192 hr at 105 degrees
3		400 degree semicoke from fresh coal
4.		400 degree semicoke from oxidized coal
5.		550 degree semicoke from fresh coal
6		550 degree semicoke from oxidized coal
7.	P-304	Devco bituminous coal, fresh
8.		Oxidized 24 hr at 105 degrees
9.		Oxidized 96 hr at 105 degrees
10.		Oxidized 168 hr at 105 degrees
11.	P-309	Phalen seam bituminous coal, coded 0 (8.34 % O)
12.	P-310	Phalen seam bituminous coal, coded 3 (7.54 % O)
13.	P-314	Phalen seam bituminous coal, coded 15 (7.01 % O)
14.	P-315	Phalen seam bituminous coal, coded 18 (6.79 % O)
15.	P-317	Phalen seam bituminous coal, coded 24 (6.22 % O)
16.	P-624	Balmer bituminous coal, fresh
17.	P-648	Bituminous coal, fresh (ERL ID #N8233)
18.	P-649	Bituminous coal, fresh (ERL ID #N8237)
19.	P-650	Bituminous coal, identified as Seam 20, adit 14
20.	P-651	Kaiser Resources (B.C.) bituminous coal
21.	P-651 Fl.S.G. 1.3	Fraction of above floats at S. G. 1.3, 20 mesh
22.		60 mesh sample of above
23.	P-651 S S.G. 1.3	Fraction of above sinks at S. G. 1.3, 20 mesh
24.		60 mesh sample of above
25.	P-668	Sub-bituminous coal sample
26.	P-668-2	Sub-bituminous coal oxidized 2 days at 105 degrees
27.	P-668-5	Sub-bituminous coal oxidized 5 days at 105 degrees
28.	P-668-7	Sub-bituminous coal oxidized 7 days at 105 degrees

OXIDATION AND WEATHERING OF BITUMINOUS COALS
INTRODUCTION AND REVIEW OF PREVIOUS STUDIES USING INFRARED SPECTROSCOPY AND/OR CLASSICAL CHEMICAL ANALYSES

In this section of the report, a concise summary of previous work is presented, indicating a continuing lack of consensus about the added functionality in artificially oxidized or naturally weathered coals.

Previous studies have explored a variety of different coals, oxidized at a variety of different temperatures from ambient to approximately 200 degrees, and part of the lack of agreement on the nature of added oxygen may thus reflect coal-dependent and temperature-dependent phenomena.

Durie and his co-workers (1) reported in 1963 that oxidation of an Australian vitrain at 170 and at 190 degrees led eventually to the virtual disappearance of aliphatic structures and the appearance of aromatic carboxylic acid groups. At earlier stages of oxidation, Painter and his co-workers (2) concluded that oxidation of PSOC-337 bituminous coal at 150 degrees generates carboxylate (-CO2-) and carbonyl (probably aryl alkyl ketonic) groups at the expense of methylene groups, while Bouwman and Freriks (3) concluded from an FTIR study of samples from a coal storage pile which had undergone spontaneous heating that carboxylic acid groups were generated.

Albers, Lenart, and Oerlert (4) suggested that increases in carbonyl content (assumed quinonoid) and in non-reactive oxygen (with little change in hydroxyl groups) occurred on oxidation of two bituminous coals at 129 and at 148 degrees.

In recently reported work, Liotta and his colleagues (5,6) have claimed that ether linkages are generated from ambient-temperature weathering of Illinois No. 6 bituminous coal.

DeVries, Bokhoven, and Dormans (7) found that wet analytical techniques indicated increases in acidic hydroxyl, carboxylic acid, and ketonic groups accompanying oxidations of two bituminous coals at 100 degrees. Berkowitz and his colleagues (8) report that aerial oxidation of Western Canadian bituminous coals generates ketonic forms, with virtually no increase in acidic oxygen-containing groups. Nandi, Montgomery, and their co-workers (9) reported that the carbonyl (ketone or quinone) of Balmer 10 low-volatile bituminous coal is unchanged after oxidation at 100 degrees for 3 days, and no carboxylic acidity is detectable, although the brief oxidation eliminates the swelling properties of the coal.

It was suggested that the small amount of additional oxygen was in the form of crosslinking ether groups.

In the past year, other studies of coal oxidation at between 150 and 300 degrees have been published (Griffiths and co-workers (10), Fuller and Smyrl (11)) using diffuse reflectance infrared Fourier Transform (D R I F T) spectroscopy. Their results are in concordance with the early work by Durie and co-workers (1); the major additional pieces of information are assignments of high-frequency carbonyl infrared absorptions to carboxylic acid anhydride and/or aryl carbonate functions.

More recently, Lin and his colleagues (12) were unable to detect (via DRIFT spectroscopy) the development of carbonyl absorptions at the expense of aliphatic bands until artificial oxidation was quite extensive.

In the most recent communication on FTIR studies of coal, Tooke and Grint (13) have examined coals oxidized in the temperature range 125-325 degrees C, and they have ascribed peaks at 1680 cm.-1 in supposedly unoxidized coal to aromatic aldehyde functions. They have attempted self-deconvolution of the difference spectra at varying oxidation temperatures, but the major features represented therein reflect differing portions of water vapor in the KBr pellets used for sample dispersion.

Although the experimental conditions in many of these studies differ, it should be noted that even for apparently similar experiments with different coals, important experimental variables (such as the degree of subdivision of the coal, the flow rate of the oxidizing air, the extent of access of the coal to air) were often not controlled or were not specified.

A significant criticism of the proposals concerning the nature of increased oxygen functionality in the artificial oxidation experiments is that they are excessively simplistic. Surely, the complex nature of coal, with the presence of differing types of polycyclic aromatic and hydroaromatic ring systems bearing differing proportions of hydroxy or ether linkages, with interconnection (and possible cross-linking) of ring systems by aliphatic chains of variable lengths, is likely to yield a variety of added oxygen functionalities.

Further, although some postulates (9,11) account for changes in the properties of coals accompanying oxidation in terms of added cross-linking, these neglect the realities that the coals are rigid structures at the experimental temperatures, and cross-linking reactions involving significant motion within such structures (such as dehydrative condensation of adjacent phenolic moieties to form diaryl ethers, or successive hydrogen-abstraction and radical recombination reactions to yield aralkyl ethers) should be regarded sceptically in the absence of conclusive experimental support.

REFERENCES

1. R. B. Conrow, R. A. Durie, J. S. Shannon, and S. Sternhell, Fuel, 42, 275 (1963).

2. P. C. Painter, M. M. Coleman, R. W. Snyder, O. Mahajan, M. Komatsu, and P. L. Walker, Applied Spectroscopy, 35, 106 (1981).

3. R. Bouwman and I. L. C. Freriks, Fuel, 59, 315 (1980).

4. G. Albers, L. Lenart, and H. Oerlert, Fuel, 53, 47 (1974).

5. R. Liotta, G. Brons, and J. Isaacs, Abstract A27, pp. 157-162. International Conference on Coal Science, Dusseldorf, September 1981.

6. R. Liotta, G. Brons, and J. Isaacs, Fuel, 62, 781 (1983).

7. H. A. W. DeVries, C. Bokhoven, and H. N. M. Dormans, Brennstoff-Chemie, 50, 289 (1969).

8. N. Berkowitz, J. F. Fryer, B. S. Ignasiak, and A. J. Szladow, Fuel, 53, 141 (1974).

9. H. M. Wachowska, B. N. Nandi, and D. S. Montgomery, Fuel, 53, 212 (1974).

10. P. R. Griffiths, S. Wang, I. M. Hamadeh, P. W. Yang and D. E. Henry, Preprints, Division of Fuel Chemistry, American Chemical Society, Vol. 28, No. 1, p. 27 (1983).

11. E. L. Fuller, Jr., Editor. Coal and Coal products: Analytical Characterization Techniques. ACS Symposium Series, No. 205, p. 133 (1983).

12. M. C. Lin, F. E. Huggins, G. P. Huffman, and D. E. Lowenhaut, Abstract FUEL53, 186th American Chemical Society National Meeting, Washington, D.C., U.S.A., August 1983.

13. P. B. Tooke and A. Grint, Fuel, 62, 1003 (1983).

PROPOSED MECHANISMS OF AERIAL OXIDATION OF COALS BASED UPON PAIFT STUDIES OF DERIVATIZED COALS

A PRIORI, the rate of oxidation of a coal will be primarily dependent upon the following:

A. Chemical factors:

1. the ratio of aliphatic carbon alpha to aromatic rings to the total carbon;
2. the proportion of hydroxy-substitution present on aromatic rings;
3. the degree and distribution of ring condensation of the aromatic rings;
4. the average chain length and distribution about the average for aliphatically linked carbon.

B. Physical factors

1. Temperature;
2. Degree of subdivision of the coal;
3. Flow rate of oxidizing species;
4. Nature of oxidizing species (air or oxygen, dry or moist).

If we regard a prototypical coal as having the idealized structure of

Ar.(CH2)n.Ar

then the most probable sites of radical formation are adjacent to the aromatic rings, leading by addition of oxygen to the alpha-peroxy radical species

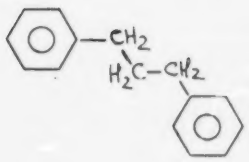
Ar.(CH.O-O.)(CH2)n-1.Ar

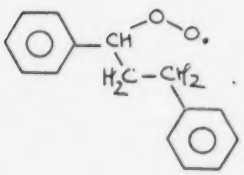
which may abstract hydrogen from further along the chain, or from an adjacent chain, to form the hydroperoxy species with a radical center further along the chain or at an adjacent chain. Reaction with a further oxygen molecule would give a hydroperoxy - peroxy species, e.g.

Ar.(CH.O-OH).CH2.(CH.O-O.).(CH2)n-3.Ar

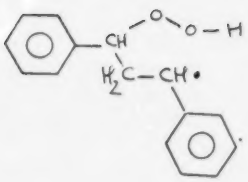
This may fragment into a ketonic species and a carboxylic acid species, accounting for the evidence of concurrent formation of both species at fairly early stages of moderate-temperature coal oxidation.

The suggested mechanism for this process is illustrated in the accompanying figure. It is based upon analogies with the high-temperature oxidative fragmentation of long-chain alkane species.

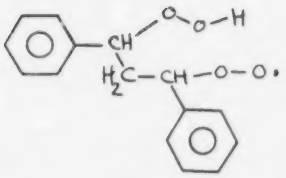




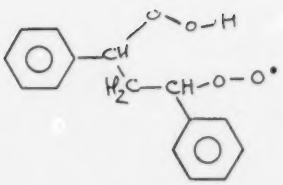
PEROXY RADICAL



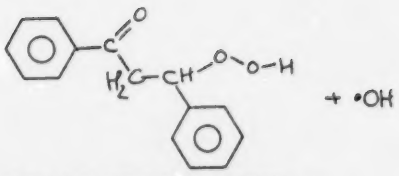
(HYDROPEROXIDE + RADICAL)



ALPHA HYDROPEROXIDE
GAMMA PEROXY

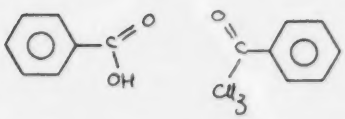


ALPHA HYDROPEROXIDE
GAMMA PEROXY



ALPHA-KETO GAMMA-HYDROPEROXIDE

ALPHA, GAMMA CLEAVAGE



AROIC ACID ARYL METHYL KETONE

POSTULATED MECHANISM BASED ON

S. KORCEK ET AL.

J. AM. CHEM. SOC. 103, 1742-1749 (1981)

Simultaneously with fragmentation, conversion of simple monohydroperoxides into aryl alkyl ketones and of diaryl ketones will occur.
Very recent work on the oxidation of alkylbenzene derivatives (see M. Pasternak and A. Morduchowitz, Tetrahedron Letters, Vol. 24, No. 40, 4275-4278 (1983)) confirms that the primary reaction point in such species is always a benzylic position.

As oxidation proceeds, the proportion of carboxylic acid species relative to the aryl alkyl ketones will increase, and at fairly advanced stages, many of the aromatic carboxylic acid groups should come to occupy adjacent (ortho) positions on the remaining aromatic skeletons.

If oxidation is performed at temperatures high enough for spontaneous dehydration of such ortho-related carboxylic acid groups, anhydrides of the type of phthalic anhydride should form readily.

The frequencies of maximal absorption of introduced carbonyl oxygen in the oxidized coals are distributed as unresolved envelopes between 1600 and 1800 cm.-1, but individual peaks are revealed by the device of quantitative methylation (as developed from previous work at St. Francis Xavier University). The approximate peak maxima in such methylated oxidized coals are found at the following positions for the various groups:

GROUP	FREQUENCY (cm.-1)
Vicinal Methoxycarbonyl	1730-1735
Isolated Methoxycarbonyl	1715-1720
Aryl alkyl ketone where aryl group lacks methoxy functions	1695-1705
Aryl alkyl ketone where aryl group carries methoxy functions	1670-1685
Diaryl ketone or anthrone type	1635-1650

ASSESSMENTS OF RELATIVE LEVELS OF OXIDATION IN BITUMINOUS COALS

The suite of samples representing a sequence of profiled oxygen levels in the samples P-317 through P-309 provides an excellent test series for the demonstration of various methods indicating correlations of various spectral parameters with varying oxygen content.

Typical PAIFT spectra are reproduced in the Figures 309-1 through P-317-10 (see page 14 for listing).

Figure P-309-1 includes the spectra of the most extensively weathered sample (P-309) and the product of its quantitative methylation. Figure P309-2 shows the increasing asymmetry of the 1600 cm.-1 band feature with increasing oxygen content of the samples, and the following Table (pg. 17) lists the relative integrated intensities in the 1600-1800 cm.-1 region (which will be dependent upon the amount of carbonyl group content in the sample) and the directly determined oxygen contents. The two quantities are linearly related to such an extent that 99 % of the changes in relative intensity in the indicated spectral region are predicted by changing oxygen content.

THUS, FOR THESE NATURALLY WEATHERED COALS, THERE IS A DIRECT LINEAR RELATIONSHIP BETWEEN AN EASILY OBSERVED SPECTRAL FEATURE AND INCREASING OXYGEN CONTENT. IT SHOULD BE NOTED THAT THIS APPROACH WILL NOT BE UNIVERSALLY APPLICABLE, BUT WILL REQUIRE INTERNAL INDIVIDUAL CALIBRATION FOR EACH COAL.

More detailed comparisons of the oxygen distribution in the various samples are available from the methylated samples. Figure P309-3 shows progressive increases in the carbonyl intensities for the series of methylations of samples P-317 through P-309; although the relationship is not precisely linear as noted for the underivatized coals, the deviations from a simple relationship arise because there are changes in the distribution of oxygen functionality among the samples. If one subtracts the PAIFT spectra of methylated P-310 from P-309 (Figure P-309-4), the major difference is centered around 1717 cm.-1 (aromatic methoxycarbonyl), whereas if a subtraction of methylated P-317 from P-310 is made (Figure P-310-7), the main difference is around 1695 cm.-1 (alkyl aryl ketone) with a secondary feature at 1718 cm.-1.

The enhanced resolvability of peak features accompanying methylation has the tradeoff in that the simple correlation of peak intensity with oxygen content is lost.

The subtraction technique may be applied to the underivatized coals (see Figure 309-5, comparing samples P-309 with P-317), but is less informative.
The remaining Figures are provided for completion, but require no added comment.

Generally similar patterns of behavior may be observed for artificial oxidations of bituminous coals. Thus, oxidation of a Devco bituminous coal at 100 degrees in a flow system resulted in an increase of oxygen content from 10.22 % to 11.90 % after 120 hours oxidation, with an increasing high-frequency asymmetry in the 1600 cm.-1 region of the PAIFT spectra with progressing time of oxidation. This is illustrated in the following Figures (DEVCO-1 and DEVCO-2).
The PAIFT spectra of methylated derivatives of artificially oxidized samples of the Balmer bituminous coal P-624, oxidized at 105 degrees for up to 336 h, exhibit a good linear relationship with the time of oxidation.
The following Table, and Figure P-624-1, illustrate this:

TABLE 2

BALMER BITUMINOUS COAL, P-624

RELATIONSHIP BETWEEN INTEGRATED CARBONYL INTENSITY AND TIME OF OXIDATION

TIME (H)	CARBONYL INTENSITY(RELATIVE)	
	OBSERVED	CALCULATED
0	1.00	1.04
48	1.15	1.10
120	1.18	1.21
336	1.55	1.54

RELATIVE CARBONYL INTENSITY = 1.04 + 0.00154(TIME OF OXIDATION)

correlation coefficent r=0.988

The spectra of the underivatized oxidized samples of coal P-624 also exhibit progressive changes in asymmetry of the 1600 cm.-1 band with increased oxidation time, which are displayed in Figure P-624-2.

NATURAL OXIDATION PROFILE OF BITUMINOUS COALS FROM PHALEN SEAM
SAMPLES P-309,-310,-314,-315,-317

Figure P-309-1
As received and methylated samples, coal P-309
Figure P-309-2
Profile of developing asymmetry in 1600-1800 cm.-1 region in as-received coals samples P-309 through P-317
Figure P-309-3
Profile of developing carbonyl peak intensity in methylated samples with progressively increasing oxygen content (P-317 through P-309)
Figure P-309-4
Difference spectrum of methylated samples of P-309 minus P-310
Figure P-309-5
Difference spectrum of as-received samples, P-309 minus P-317
Figure P-310-6
As received and methylated samples, coal P-310
Figure P-310-7
Difference spectrum of methylated samples of P-310 minus P-317
Figure P-314-8
As received and methylated samples, coal P-314
Figure P-315-9
As received and methylated samples, coal P-315
Figure P-317-10
As received and methylated samples, coal P-317

BITUMINOUS COAL P-309

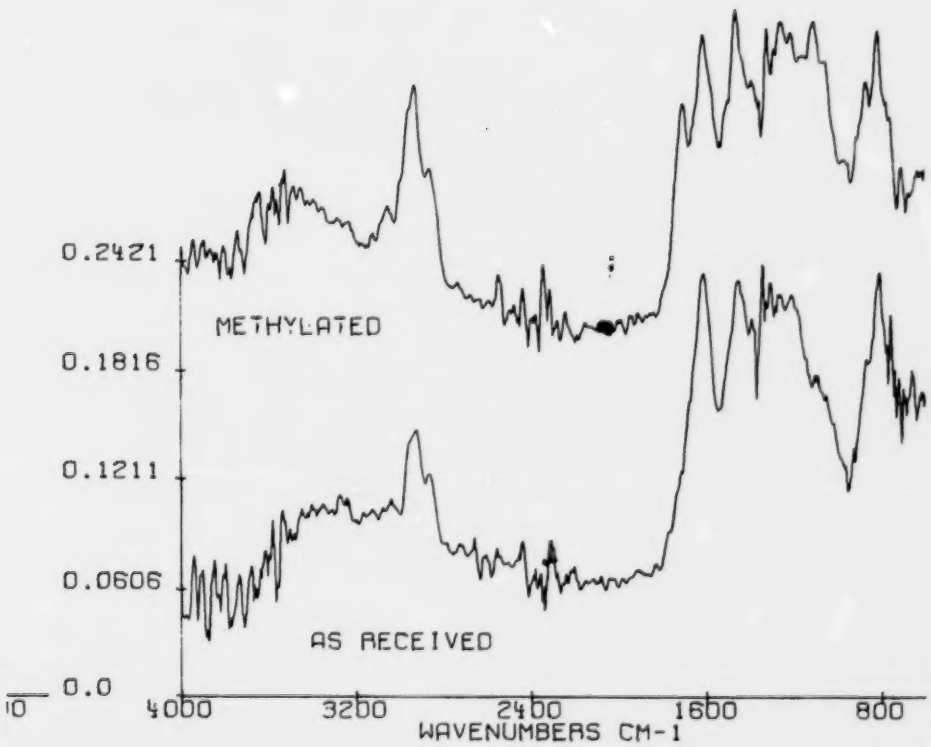


FIGURE P-309 - 1

1702.4

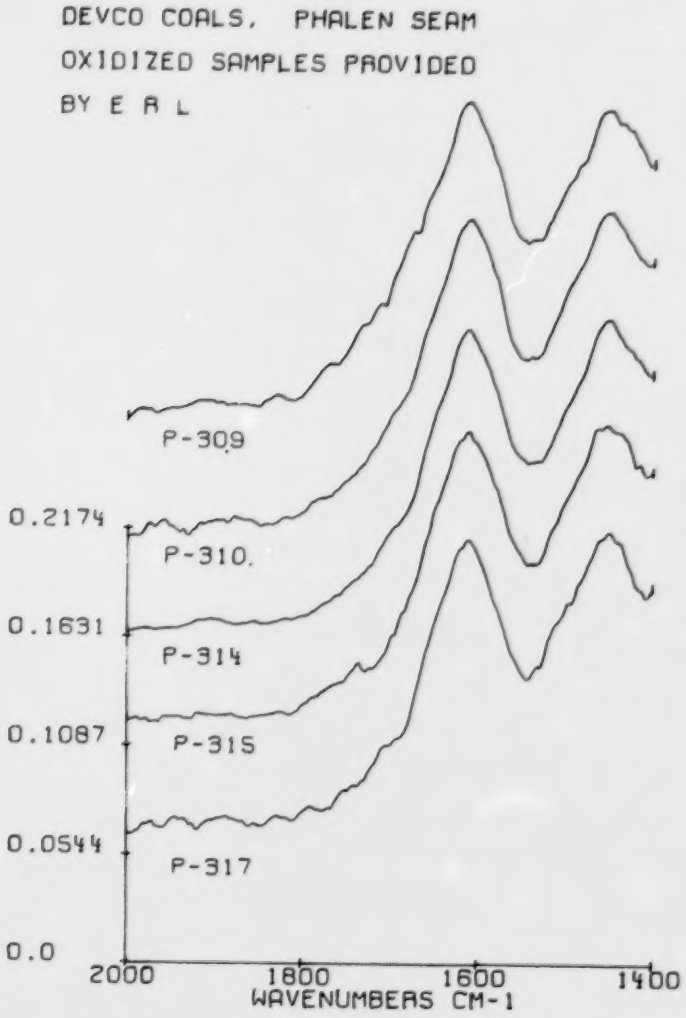


FIGURE P309- 2

TABLE 3

CORRELATION BETWEEN INTEGRATED INTENSITY OF PAIFT SPECTRA FROM 1600-1800 CM-1 WITH OXYGEN CONTENT, PHALEN SEAM BITUMINOUS COAL SAMPLES

Sample #	Intensity (relative)	Oxygen % (direct analysis)
P-317	1.0000	6.22
P-315	1.0940	6.79
P-314	1.1175	7.01
P-310	1.2440	7.54
P-309	1.4152	8.34

Intensity = -0.25 + 0.199 (Oxygen %)

r = 0.9956

Changing oxygen content predicts 99 % of the changes in intensity

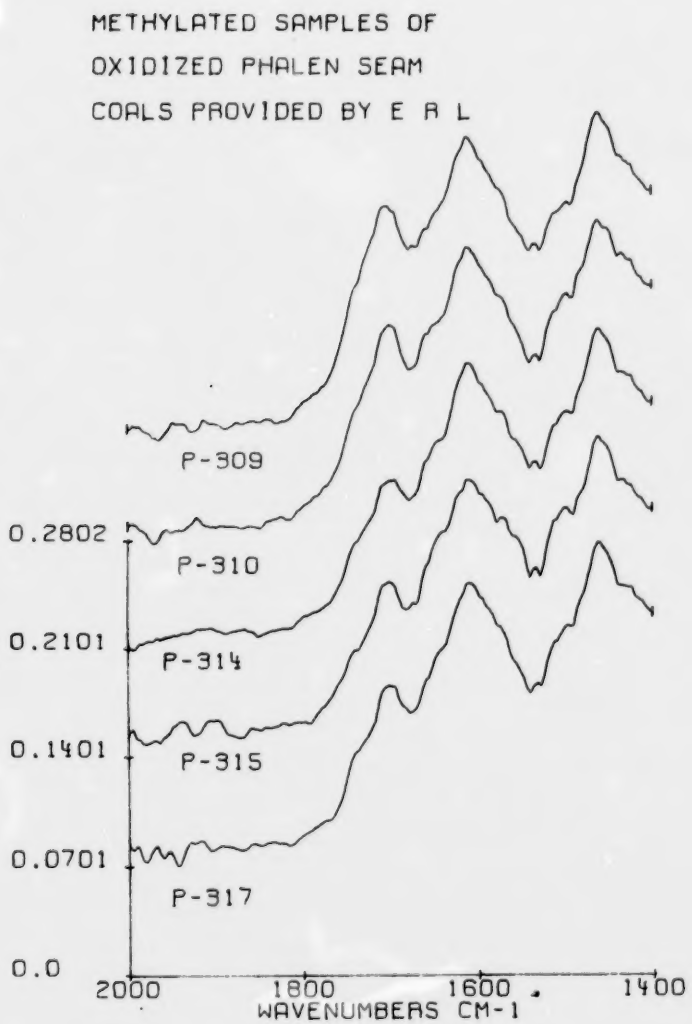


FIGURE P-309 - 3

DIFFERENCE SPECTRUM
METHYLATED

P-309 VS. P-310

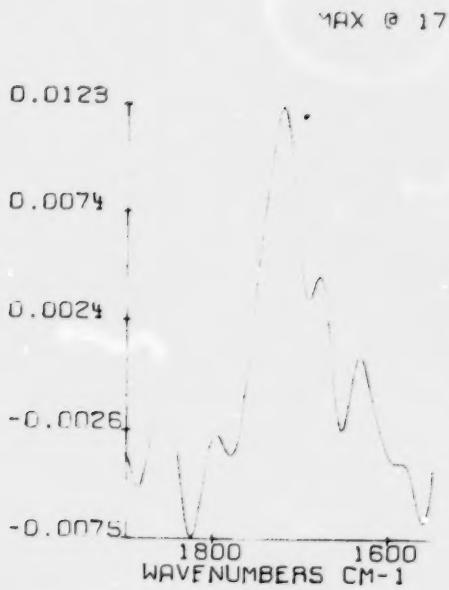


FIGURE P-309 - 4

DIFFERENCE SPECTRUM
P-309 MINUS P-317

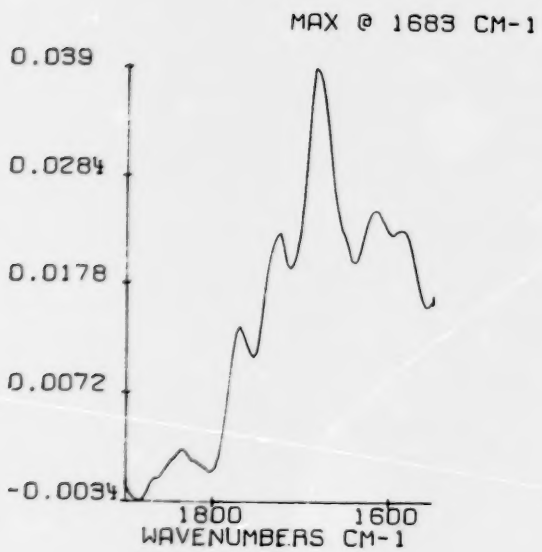


FIGURE P - 309 - 5

BITUMINOUS COAL P-310

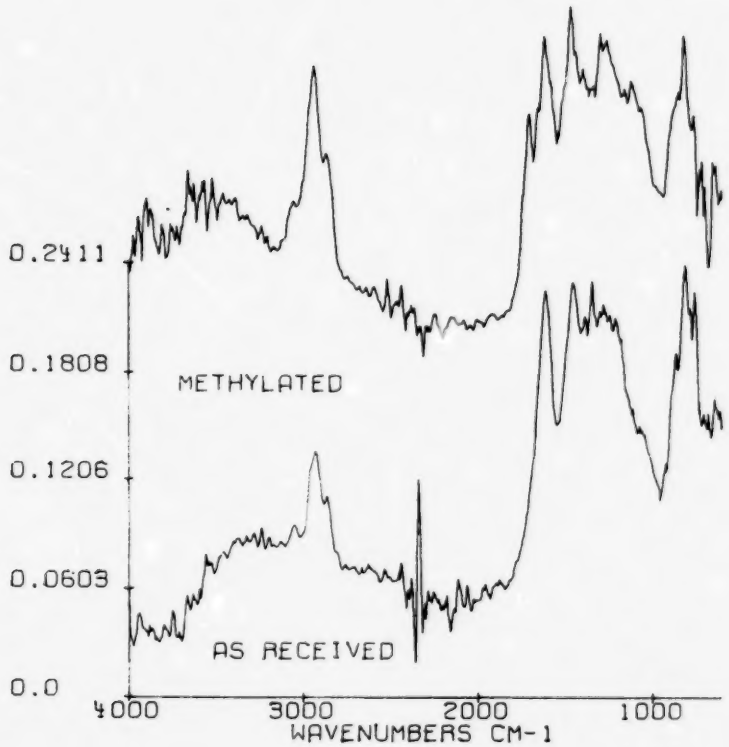


FIGURE P-310 - 6

DIFFERENCE SPECTRUM

METHYLATED P-310 VS. P-317

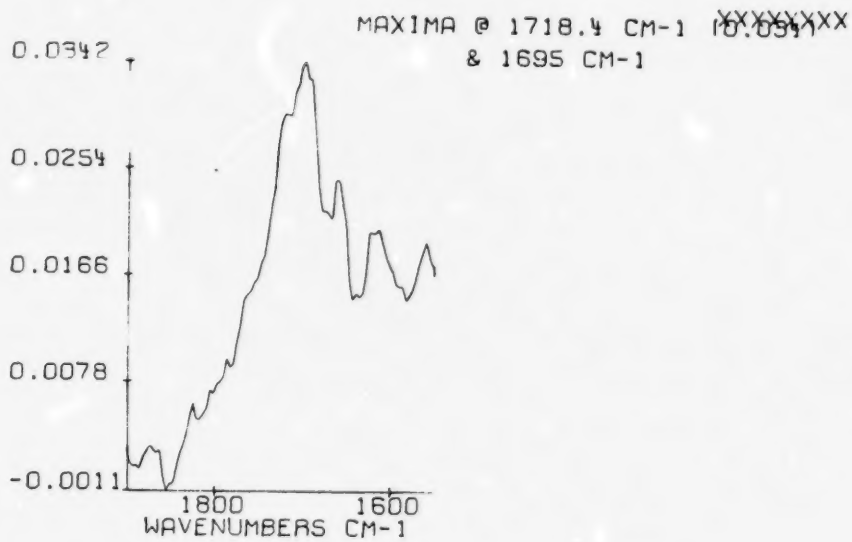


FIGURE P - 310 - 7

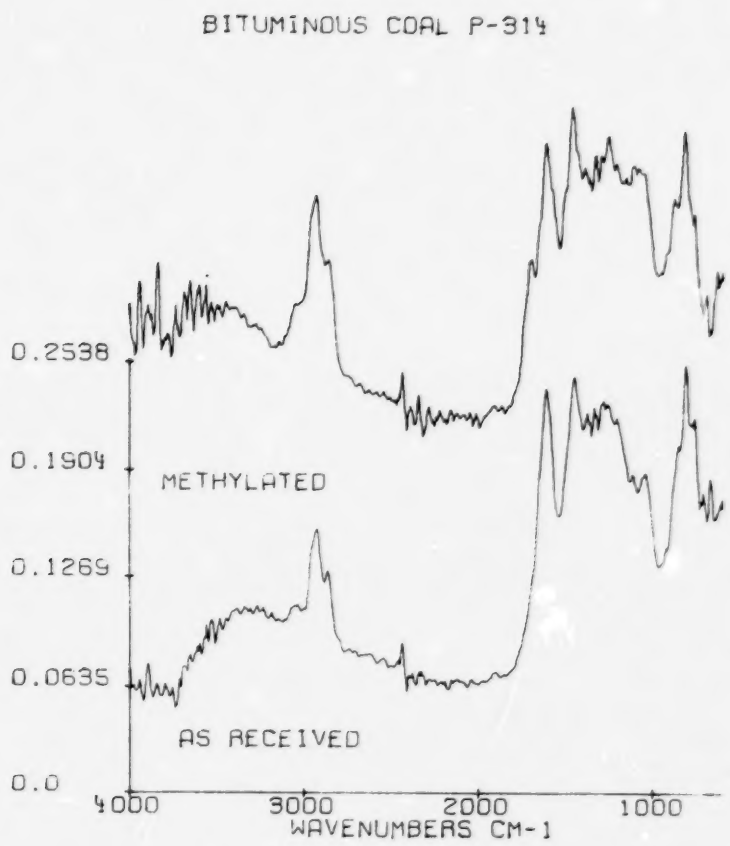


FIGURE P- 314 - 8

FIGURE P-314

BITUMINOUS COAL P-315

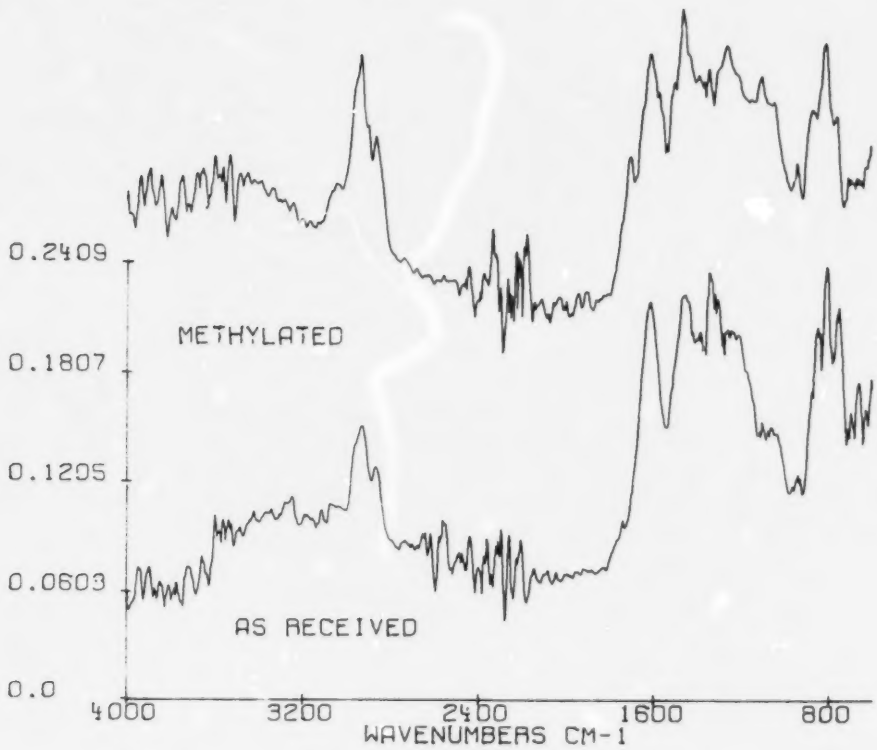


FIGURE P-315 – 9

BITUMINOUS COAL P-317

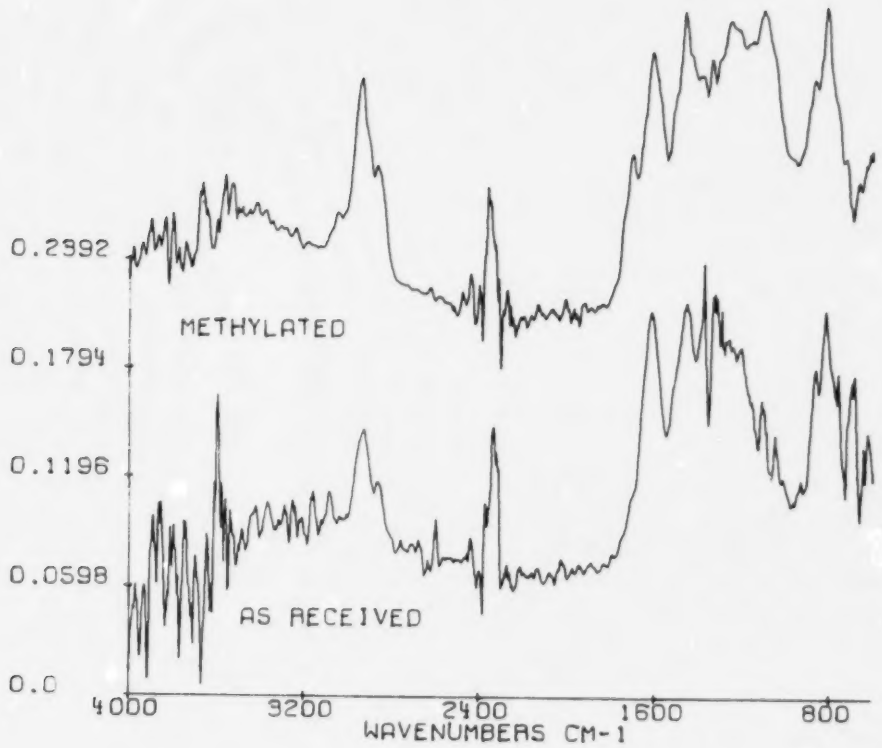


FIGURE P317 - 10

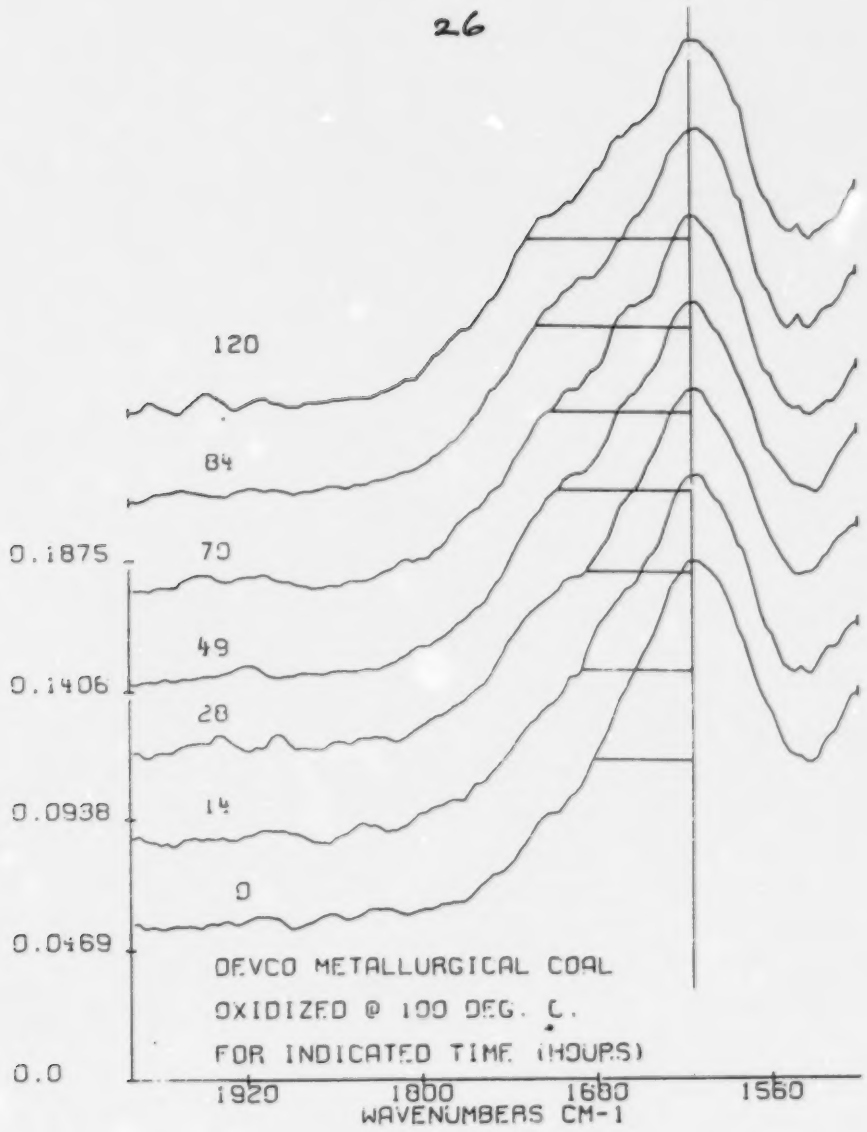


Figure DEVCO - 1

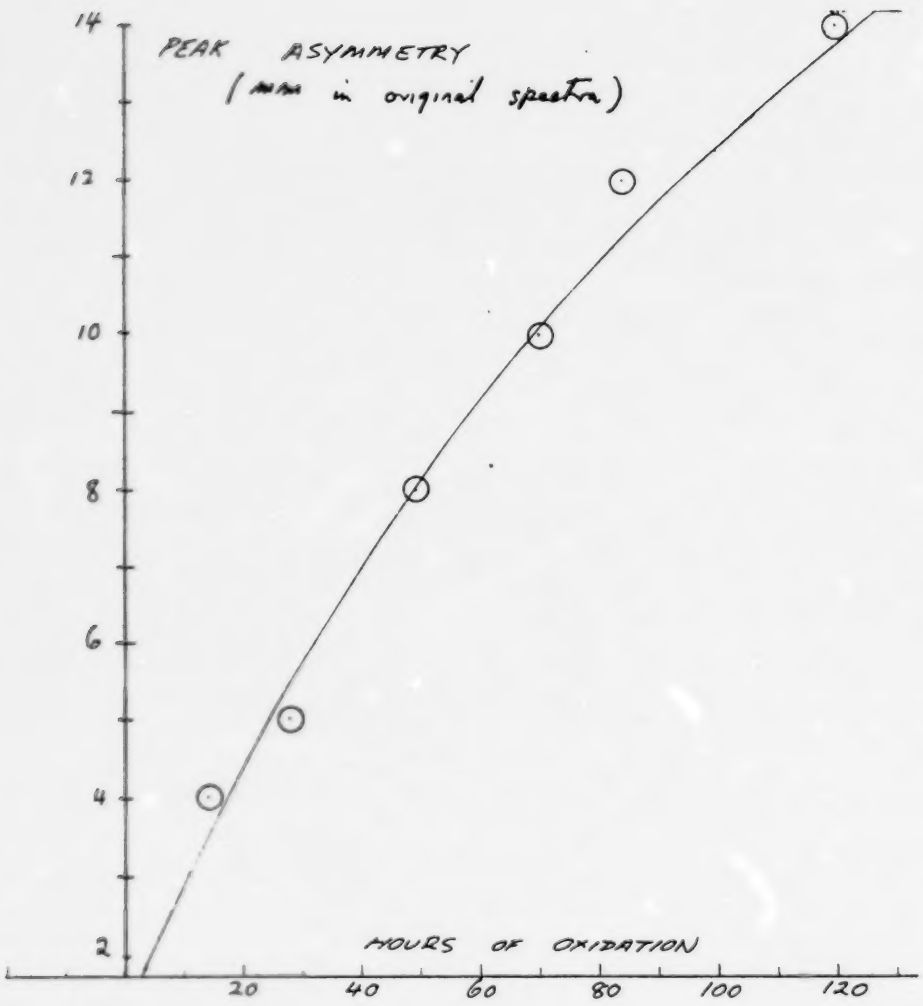


Figure DEVCO-2

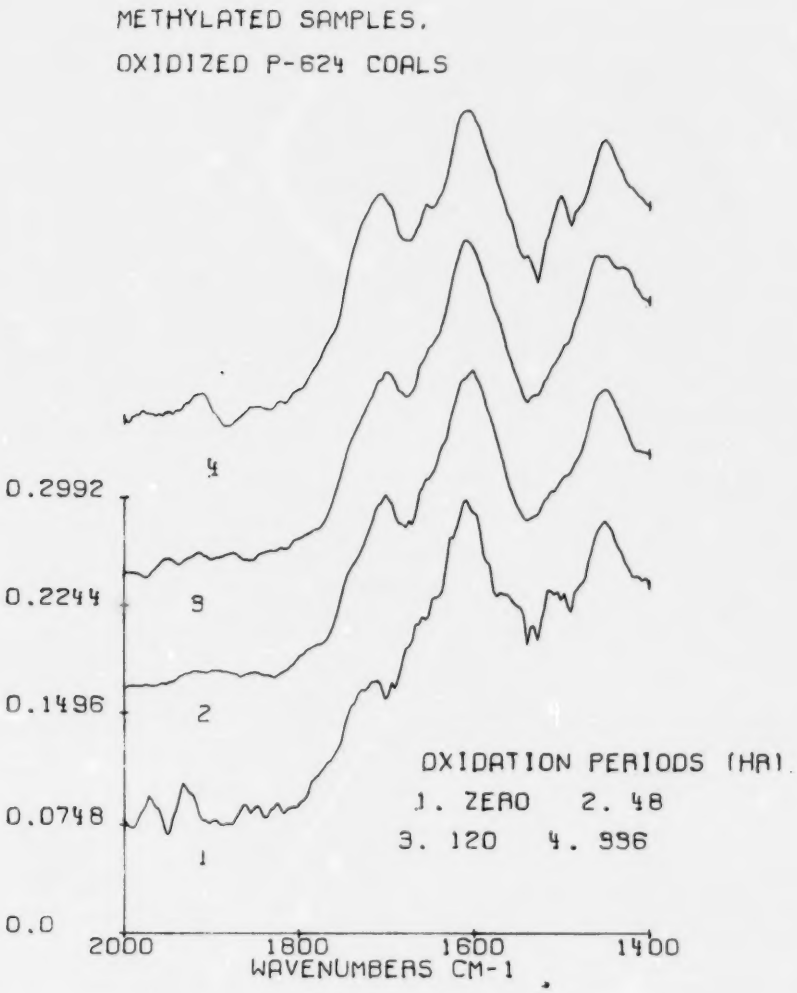


FIGURE P-624-1

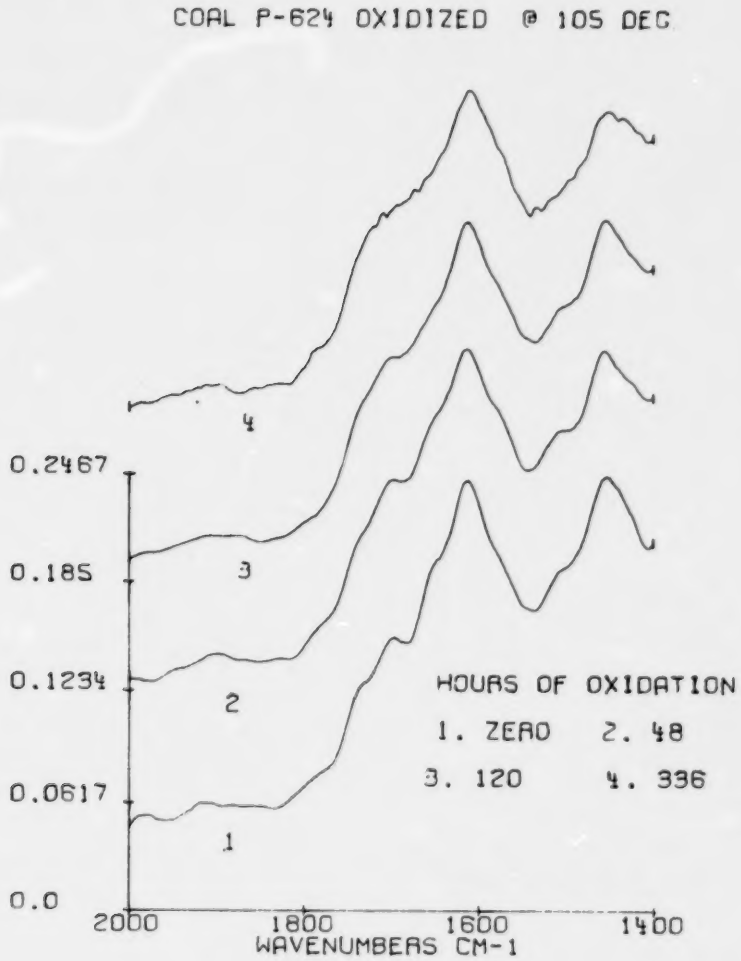


FIGURE P-624-2

SEMICOKE FORMATION FROM FRESH AND OXIDIZED BITUMINOUS COAL

BITUMINOUS COAL P-303

The parent sample of this series is a Phalen Seam coal supplied to CANMET by the Cape Breton Development Corporation.

Supplied individual samples included the "fresh" unoxidized coal, a coal oxidized at 105 degrees for 192 hours, and semicokes derived from each of these starting materials by heating to 400 degrees and 550 degrees respectively.

In addition, we were provided with sink-float separated fractions of the "fresh" coal obtained by differentiation at a specific gravity of 1.3.

The individual samples were derivatized by the standardized methylation procedure we have developed.

The PAIFT spectra are reproduced in Figures 303-1 through 303-15 as follows:

Figure 303-1: As received ("fresh") coal snd the product of quantitative methylation.

Figure 303-2: As received coal sample and the separated sink and float fractions.

Figure 303-3: Methylated samples corresponding to the materials of Figure 303-1.

Figure 303-4: Bulk oxidized coal and product of methylation.

Figure 303-5: Comparisons in 2000-1400 cm.-1 region of bulk "fresh" coal and its methylation product.

Figure 303-6: Comparisons in 2000-1400 cm.-1 region of the oxidized coal and its methylation product.

Figure 303-7: As received coal, 400 degree semicoke, and methylation product of semicoke.

Figure 303-8: Comparisons in 2000-1400 cm.-1 region of samples of figure 303-7.

Figure 303-9: Oxidized coal and its 400 degree semicoke

Figure 303-10: Comparisons in 2000-1400 cm.-1 region of oxidized coal, its 400 degree semicoke, and the "fresh" coal.

Figure 303-11: Comparsions in 2000-1400 cm-1 region of "fresh" coal, its methylation product, the 400 degree semicoke from the "fresh" coal, and its methylation product.

Figure 303-12: Comparisons in 2000-1400 cm.-1 region of oxidized coal, its methylation product, the 400 degree semicoke from the oxidized coal, and its methylation product.

Figure 303-13: Further scale expansion between 1740 and 1540 cm.-1 of spectra #2 and 4 in Figure 303-11.

Figure 303-14: As received coal and 550 degree semicoke.

Figure 303-15: Oxidized coal and 550 degree semicoke.

Figure 303-16: Difference spectra of methylated oxidized coal versus methylated as received coal

Figure 303-17: Difference spectra of methylated 400 degree semicokes from oxidized versus as received coal

DISCUSSION OF SPECTRA:

SEMICOKE FORMATION FROM FRESH AND FROM OXIDIZED BITUMINOUS COAL P-303

New evidence concerning the course of semicoke formation from thermolysis of "fresh" and of oxidized samples of bituminous coal P-303 may be adduced with the added definition of structural features obtainable after quantitative methylations of these materials.

Figure 303-1 is representative of the general changes in the PAIFT spectra of the bulk coal accompanying application of the methylation procedure to the bulk "fresh" coal; similar changes are evident in Figures 303-3, 304-4, and 304-7, showing the complete spectral range from 4000 to 600 cm.-1.

The key changes as compared with the corresponding spectra of the "fresh" coal include elimination of the broad O-H stretching absorption band and its replacement by methoxy aliphatic group absorption between 3000 and 2800 cm.-1, development of a distinct resolved peak centered at 1702 cm.-1 (assigned to an aryl alkyl ketone group), together with enhanced intensity in the aliphatic C-H deformation region around 1450 cm.-1 and in the C-O stretch region around 1050 cm.-1.

More details of the differences accompanying methylation are reproduced in the scale-enhanced Figures 303-5,-6,-8,-11,-12,-13, showing the clearly separated carbonyl absorption features. The differences are revealed very clearly by subtraction of the features in the methylated "fresh" coal from those in the methylated oxidized coal (Figure 303-16), which shows that the major difference is around 1730 cm.-1, defining that the major added functionality in the oxidized versus the "fresh" species is in the form of aromatic carboxylic acid groups.

When the 400 degree semicokes are compared with the original coals and with the methylated semicokes ("fresh" coal and derived semicokes, Figure 303-7), the principal changes accompanying the semicoke formation are increases in the relative intensity of the out-of-plane aromatic C-H deformation triplet, and decreases in peaks associated with aliphatic C-H.

The pattern for the analogous semicokes from the oxidized coal sample (see Figure 303-9) reveals similar decreases in the relative contribution from aliphatic C-H absorptions. There are more profound changes in the carbonyl-group distribution, which are revealed by subtractive procedures on the methylated semicokes. A difference spectrum on the methylated 400 degree semicokes (oxidized minus "fresh") (Figure 303-17) indicates that the major distinction between the two is no longer an additional feature around 1730 cm.-1, but has shifted to around 1710 cm.-1.

Although this observation is consistent with significant decarboxylation and the presence of remaining ketonic functionality, it is also consistent with a change in the environment of the same type of methoxycarbonyl group accompanying thermal dehydration and dehydrogenation at other parts of the coal polymer. More extensive experimentation, possibly using model compounds, would be required in order to settle this point.

The PAIFT spectra of higher-temperature semicokes, obtained by heating at 550 degrees, show little difference between oxidized and fresh source material (see Figures 303-14, 303-15); spectra of the methylated materials (not illustrated) are also almost identical.

Although the higher-temperature semicokes may have differences in their structures and compositions, the loss of the major part of the labile oxygen functionality (both carbonyl and carboxyl) leads to marked resemblances in the spectra.

FIGURE 303-1

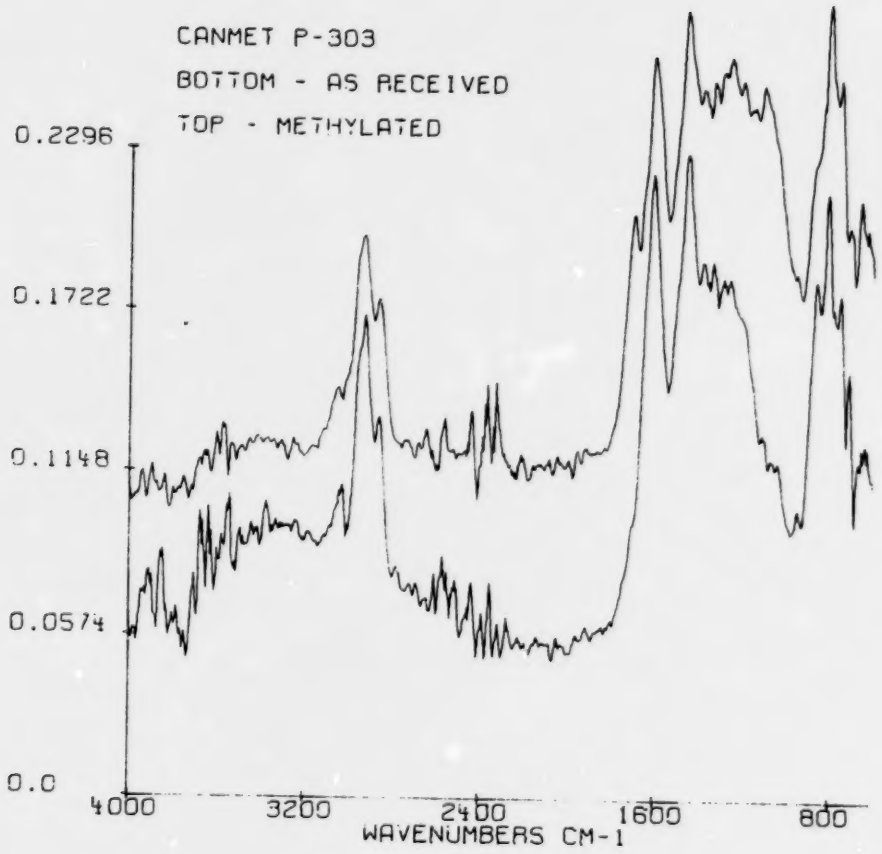

CANMET P-303
BOTTOM - AS RECEIVED
TOP - METHYLATED
0.2296
0.1722
0.1148
0.0574
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 303-2

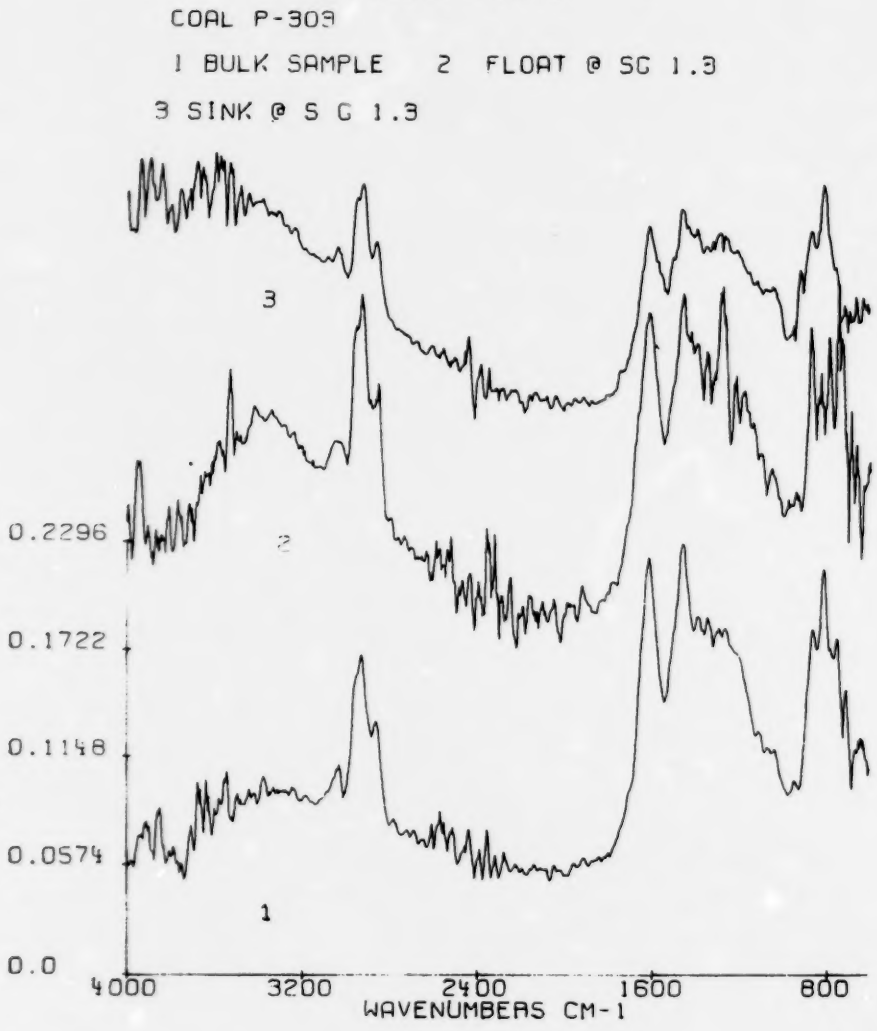

COAL P-309
1 BULK SAMPLE 2 FLOAT @ SG 1.3
3 SINK @ S G 1.3
3
2
1
0.2296
0.1722
0.1148
0.0574
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 303-3
METHYLATED SAMPLES, COAL P-309

FRACTIONS

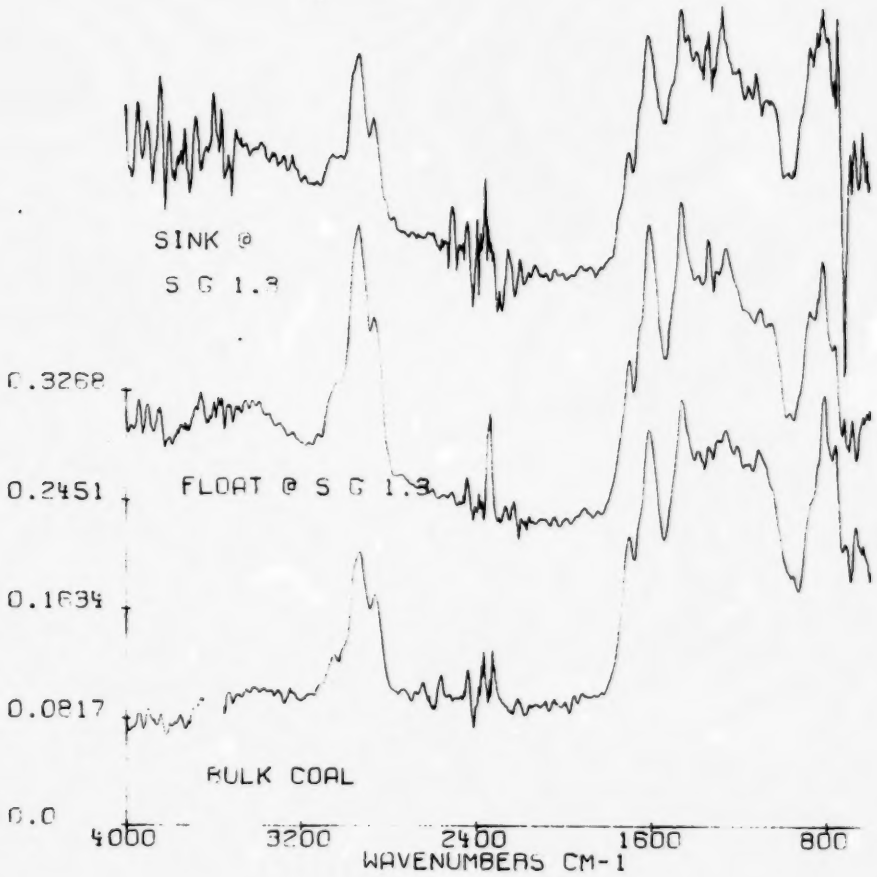


FIGURE 303-4

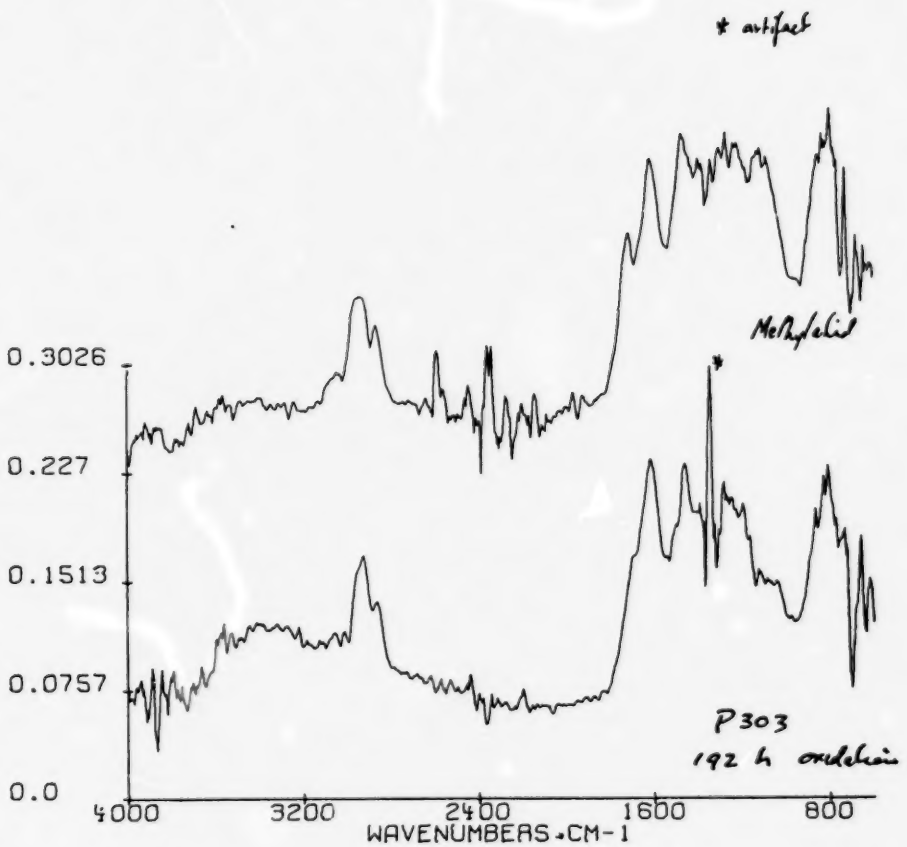

* artifact
Methylcellulose
0.3026
0.227
0.1513
0.0757
0.0
4000
3200
2400
1600
800
WAVENUMBERS-CM-1
P303
192 h oxidation

FIGURE 303-5

COAL P-303
2000-1400 CM.-1
1 BULK SAMPLE
2 SAMPLE 1 METHYLATED

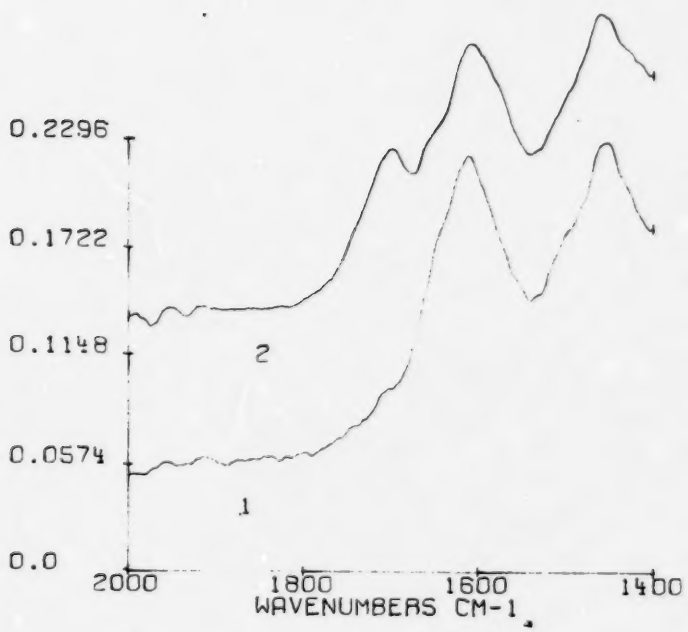


FIGURE 303-6

COAL P-303 OXIDIZED @ 105 DEG.. 192 HR.

1 OXIDIZED SAMPLE
2 SAMPLE 1 METHYLATED

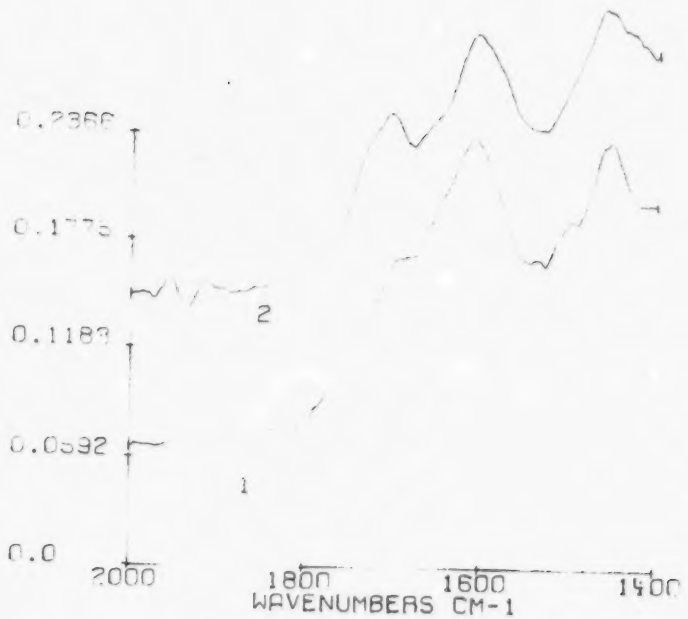
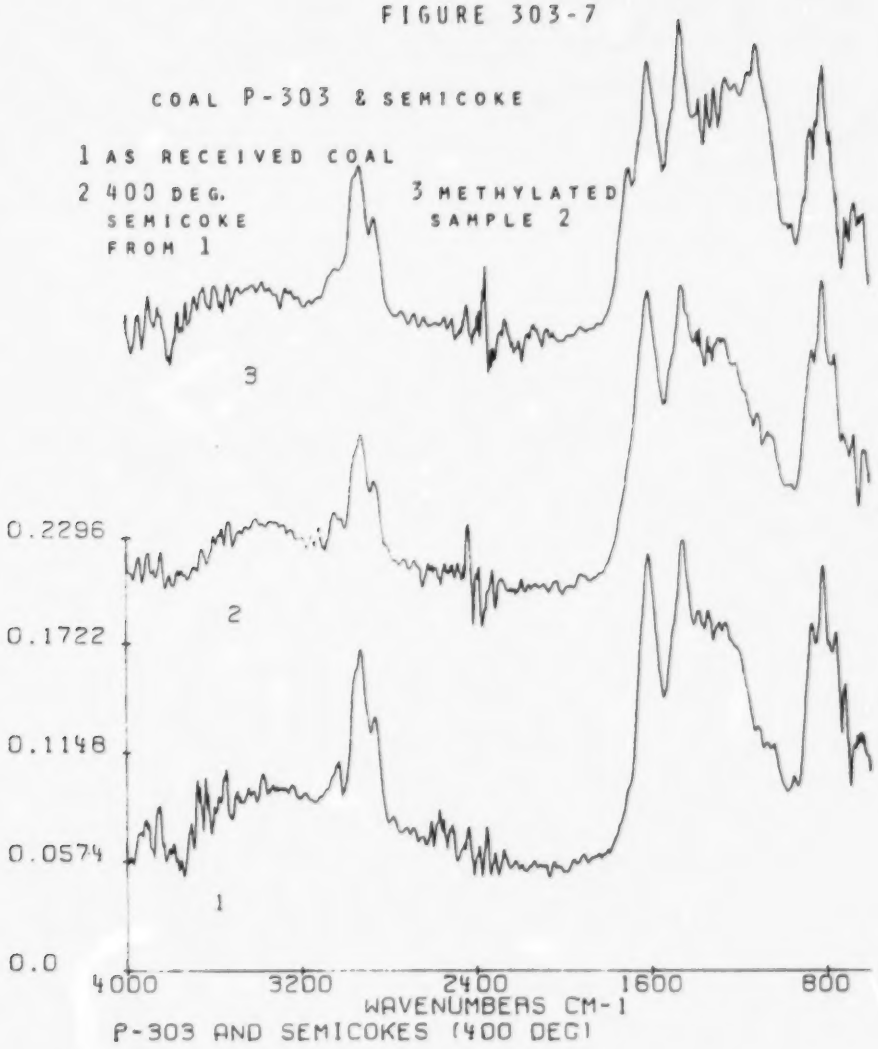


FIGURE 303-7



P-303 AND SEMICOKES (400 DEG)

FIGURE 303-8
COAL P-303 & SEMICOKES
1 AS RECEIVED COAL
2 400 DEGREE SEMICOKE FROM 1
3 METHYLATED SAMPLE 2

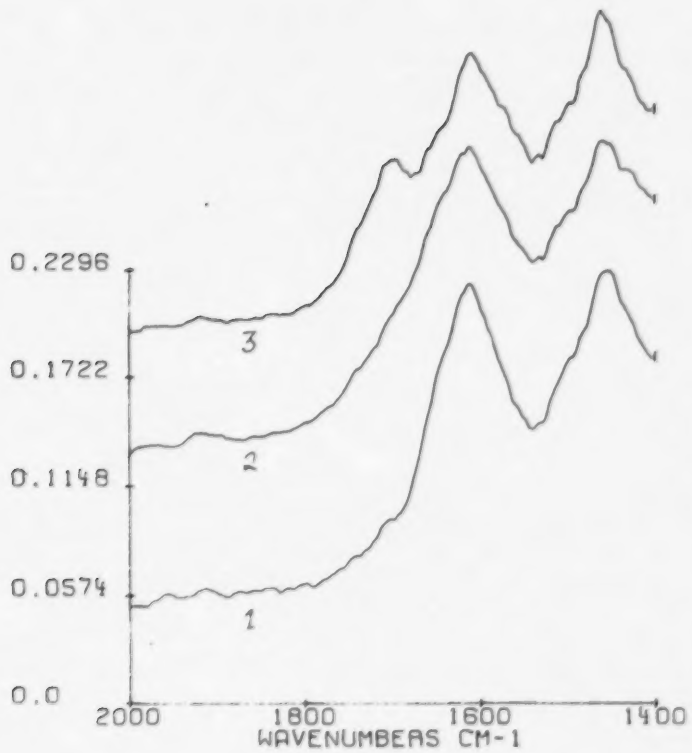


FIGURE 303-9

COAL P-303

OXIDIZED 192 HR @ 105 DEG.,

AND SEMICOKE FROM HEATING.

TO 400 DEG. C

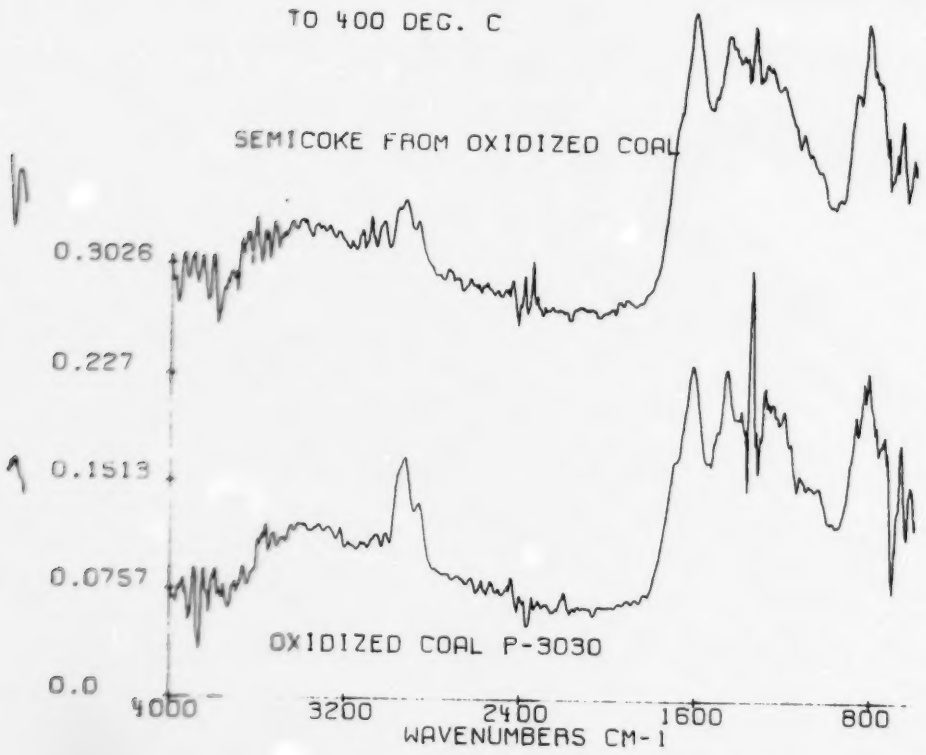


FIGURE 303-10

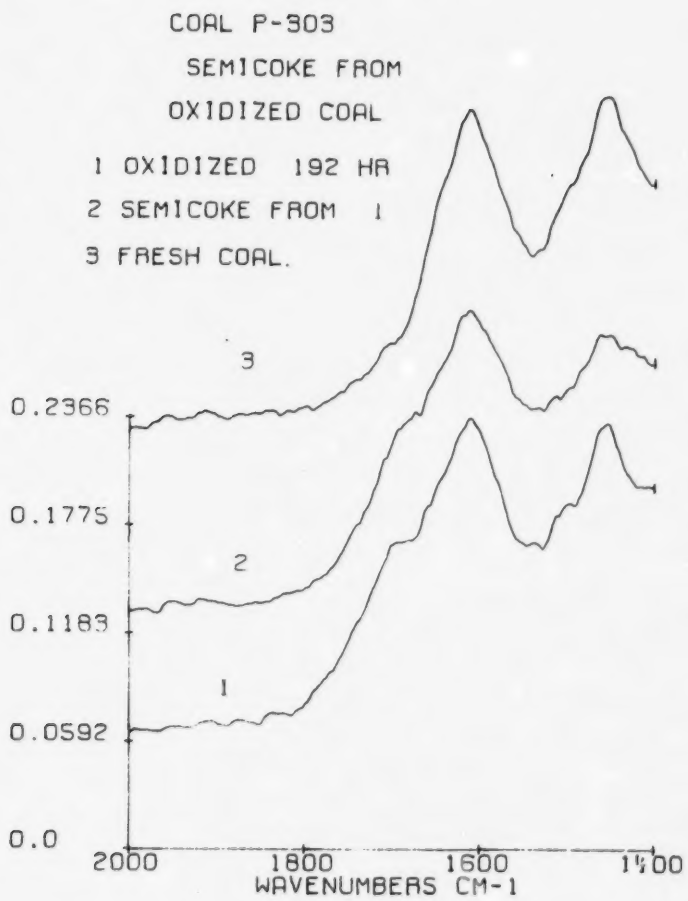


FIGURE 303-11

COAL P-309 & SEMICOKE

METHYLATED SAMPLES

1 COAL AS RECEIVED

2 SAMPLE 1 METHYLATED

3 400 DEG. SEMICOKE FROM SAMPLE 1

4 SAMPLE 3 METHYLATED

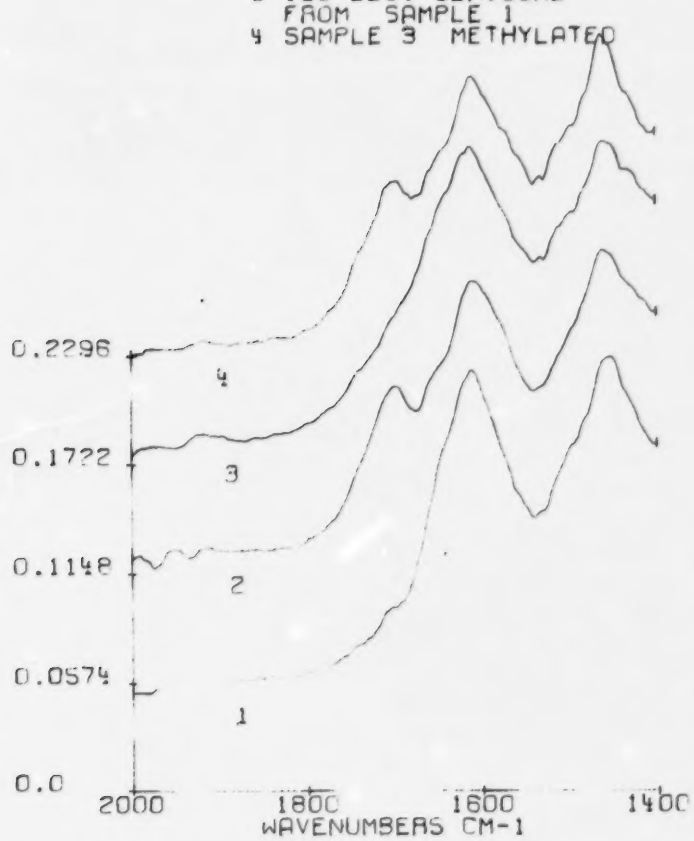


FIGURE 303-12

OXIDIZED COAL P-303 & SEMICOKES

1 AS RECEIVED OXIDIZED COAL

2 METHYLATED SAMPLE 1

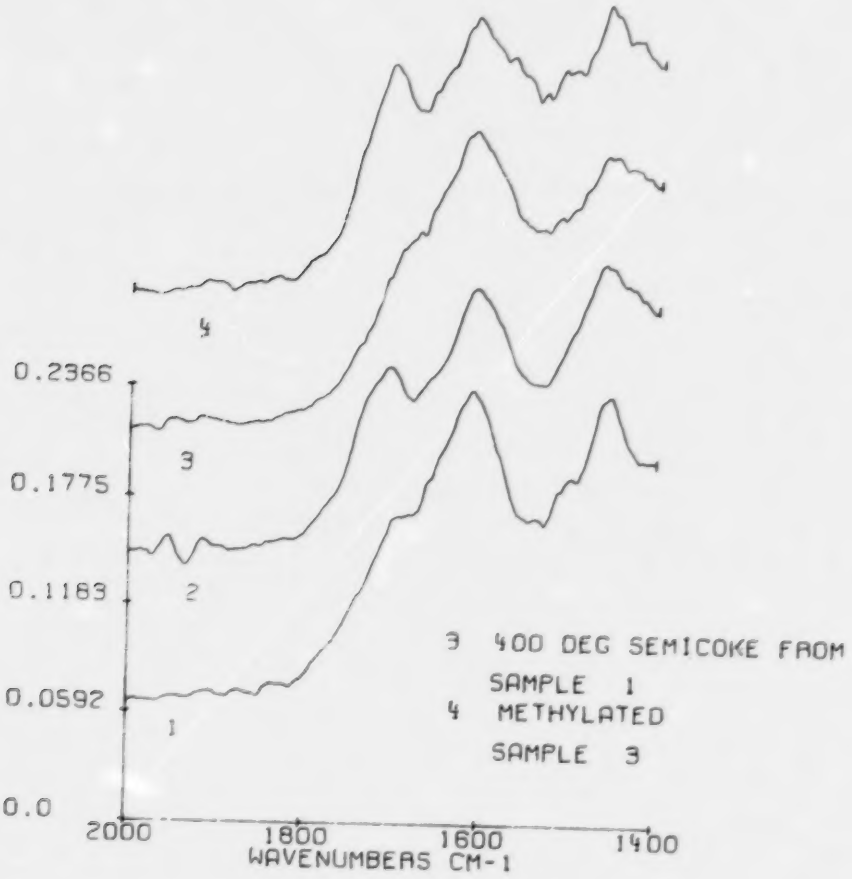


FIGURE 303-13

COAL P-303
2 METHYLATED OXIDIZED SAMPLE
4 METHYLATED 400 DEG SEMICOKE
FROM OXIDIZED P-303

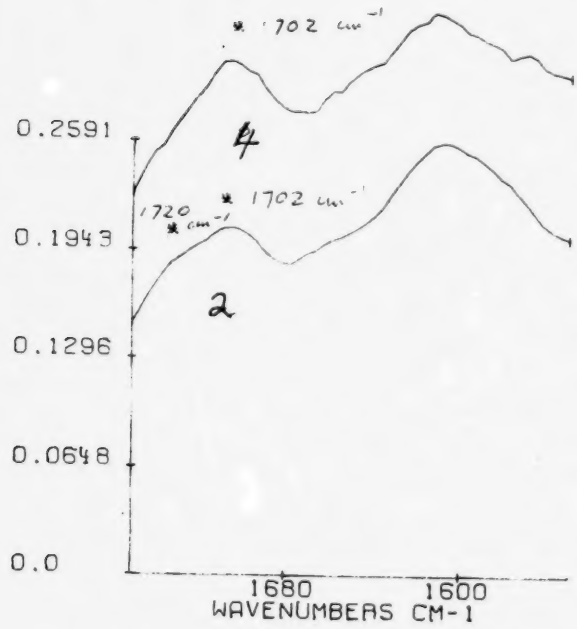


FIGURE 303-14
COAL P-303 & 550 DEGREE SEMICOKE

1 AS RECEIVED COAL

2 SEMICOKE

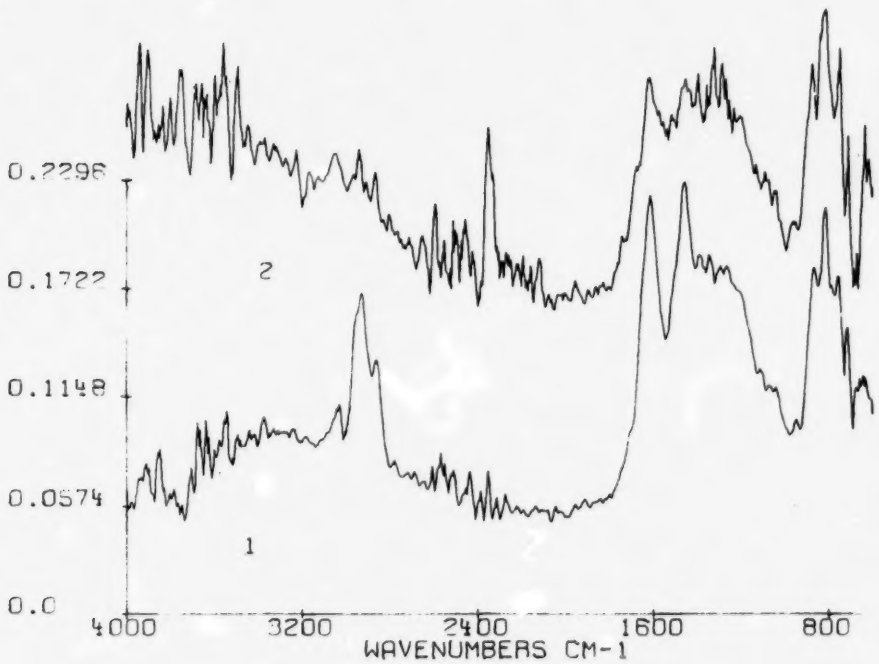


FIGURE 303-15

OXIDIZED COAL P-303
& 550 DEGREE SEMICOKE

1 OXIDIZED COAL
2 SEMICOKE

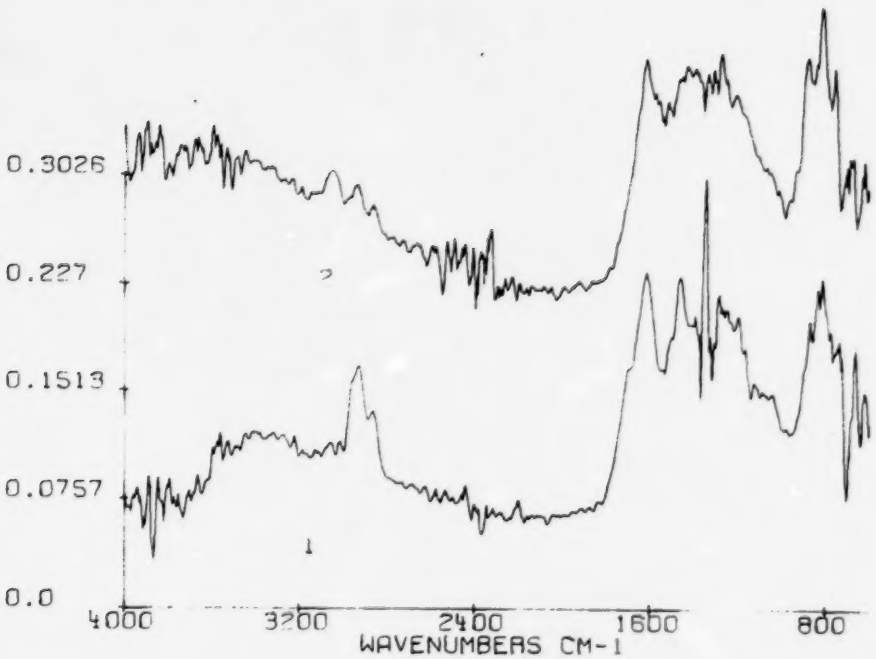


FIGURE 303-16

COAL P-903
DIFFERENCE SPECTRA
OF METHYLATED OXIDIZED COAL
(192 HR @ 105 DEG) VERSUS
METHYLATED AS RECEIVED COAL

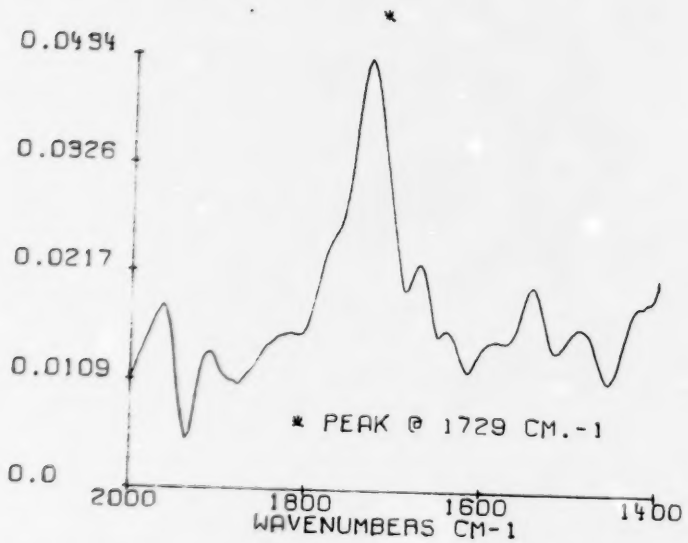
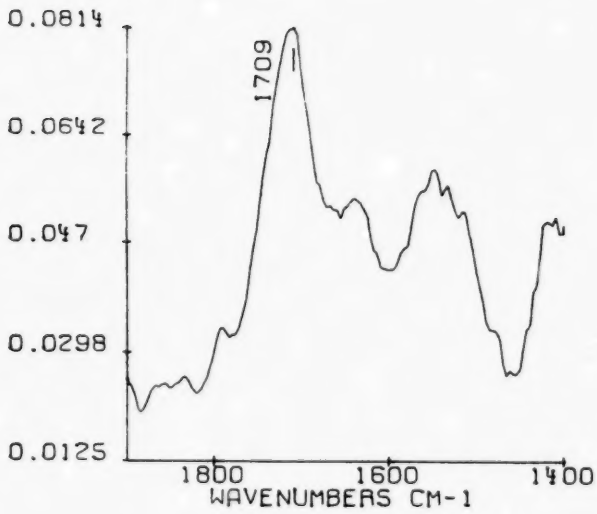


FIGURE 303-17

DIFFERENCE SPECTRA

METHYLATED P-303 SEMICOKE

OXIDIZED VS. FRESH



DISCUSSION OF TREATMENTS - KAISER RESOURCES BITUMINOUS COAL P-651

The supplied samples included the bulk coal and separated sink and float fractions.
Figure P-651-1 of this series illustrates the three spectra: the key evident feature is the dominance of the sink fraction by the siliceous mineral matter (analysis indicates this coal to contain approximately 33 % ash).

Quantitative methylation of such samples, as illustrated in Figure P-651-2, enhances the O-H stretching features characteristic of kaolinite, around 3620-3650 cm.-1 in the methylated bulk coal and the methylated sink fraction. A key feature of the spectra of such highly mineral-contaminated coals is that the aromatic C-H deformation region is distorted by kaolinite or quartz absorptions (around 800 and 700 cm.-1).

Figure P-651-3 shows that the methylated float and sink fractions have similar "normalized" spectra in the 2000-1400 cm.-1 region; this suggests that there is little actual difference between the coal constituents in the two fractions, in that the extent of oxidation as indicated by the carbonyl band intensities, and the aromatic/aliphatic ratios as adduced by the relative intensities of the 1600 cm.-1 and 1460 cm.-1 features, are very similar.

Figure P-651-4 illustrates a possible strategy to indicate the approximate proportion of alkylatable phenolic oxygen using deuterium-labelled methyl iodide. The intensities of the C-D absorptions (below 2400 cm.-1) from the perdeuteromethoxy groups may be ratioed to those of the aliphatic C-H features from 2920-2800 cm.-1. In the illustrated examples, the apparent quantity of deuterium introduced onto alkylatable phenolic hydroxy groups is about one-half that of hydrogen present on the aliphatic carbons.

Figure P-651-5 illustrates the point suggested above, showing that the demineralized sink fraction (with demineralization at room temperature) is closely similar to the float fraction.

Figure P-651-6 shows that HCl treatment has little effect on mineral-matter proportion; as expected, the primary demineralizing agent is HF.

The difference spectrum between the sink fraction and its product of demineralization (Figure P-651-7) shows a spectrum closely resembling kaolinite, indicating that the major infrared absorbing species in the mineral matter accompanying the sink fraction is this species.

Figure P-651-8 indicates the general similarity in PAIFT spectra between supplied fractions of differing initial particle sizes.

Figure P-651-9 illustrates a simulated demineralization, where 22 % of the PAIFT spectrum of the low-temperature ash from the sink fraction is subtracted from that of the original sample; it is compared with the spectrum of the sink fraction subjected to a standard chemical demineralization, involving reaction with HF at 50-55 degree. There is a reasonable correspondence between the two although the relative intensities of many peak features differ. The differences could be intra-sample in nature, or be a consequence of rearrangements or ring condensations accompanying the chemical demineralization.

Finally, Figure P-651-10 illustrates that the low-temperature ash from the sink fraction is indeed principally kaolinite; particular note should be made of the features at 791 and 698 cm.-1, which would interfere with evaluations of aromatic character from examination of the aromatic C-H out-of-plane deformation patterns.

KAISER RESOURCES BITUMINOUS COAL P-651

SINK/FLOAT FRACTIONS, METHYLATION AND DEMINERALIZATION EFFECTS

Figure P-651-1

Comparative spectra of bulk sample and sink and float fractions at s.g. 1.3

Figure P-651-2

Quantitatively methylated samples corresponding to the starting materials of Figure P651-1

Figure P-651-3

Expanded spectrum of methylated sink and float fractions in the 2000-1400 cm.-1 regions

Figure P-651-4

Float fraction, float fraction methylated, float fraction deuteromethylated

Figure P-651-5

Demineralized sink fraction (treated with HCl, then HF); float fraction

Figure P-651-6

Bulk coal, refluxed with 5M HCl, then treated with HF at room temperature for 10 days

Figure P-651-7

Difference spectrum - as received sink fraction minus demineralized sink fraction

Figure P-651-8

Float fractions, ground to differing particle sizes (200 mesh and 20 mesh)

Figure P-651-9

Comparison of chemical and "synthetic" demineralization of sink fraction

Figure P-651-10

Low-temperature ash from sink fraction (principally kaolinite)

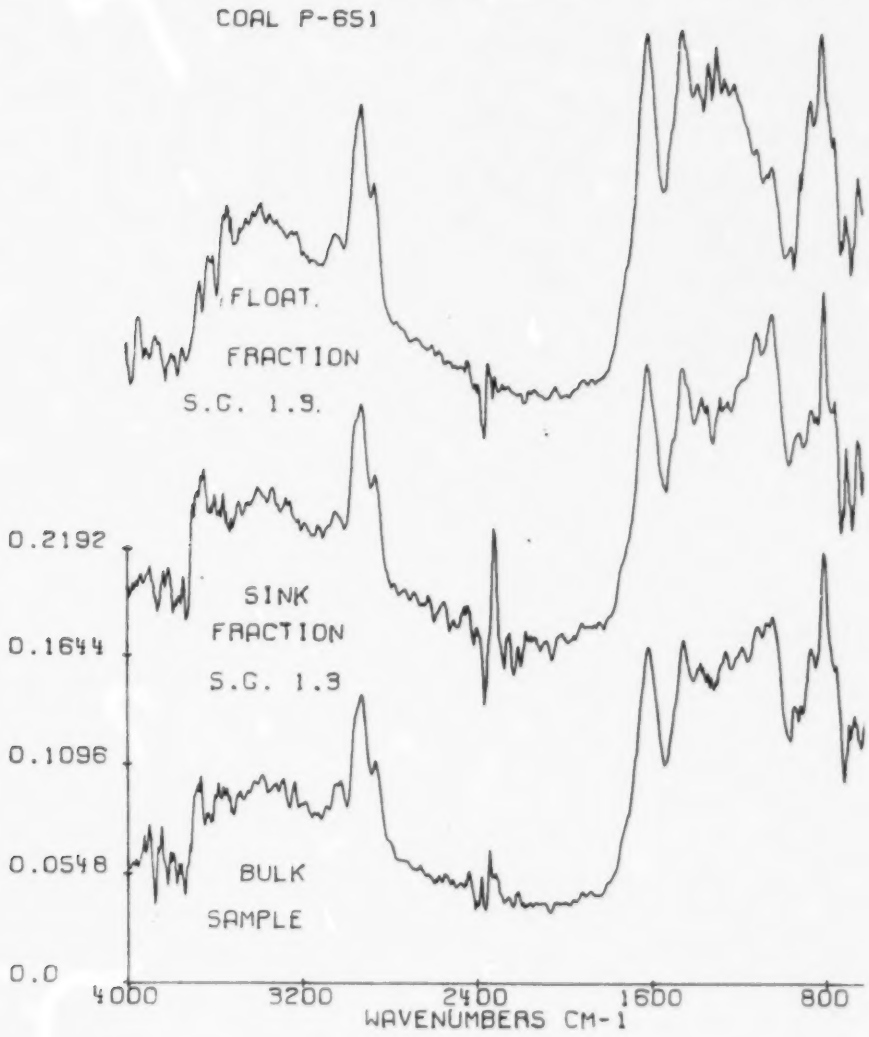


FIGURE P-651-1

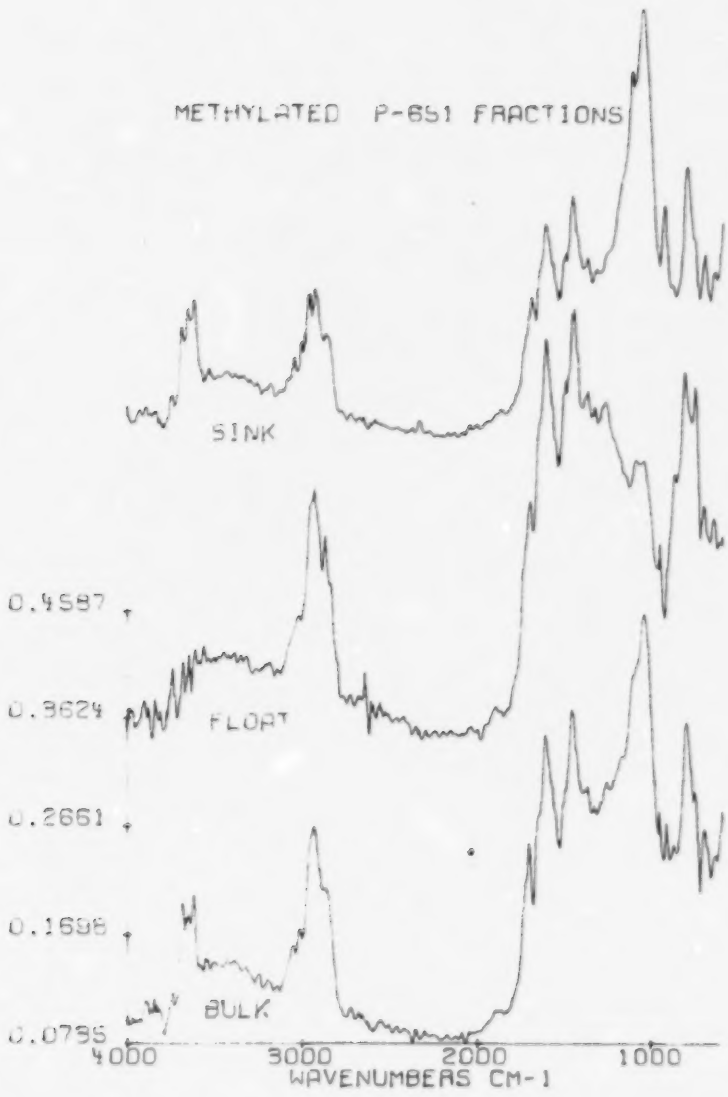


FIGURE P-651-2

P-651 COAL

METHYLATED SAMPLES

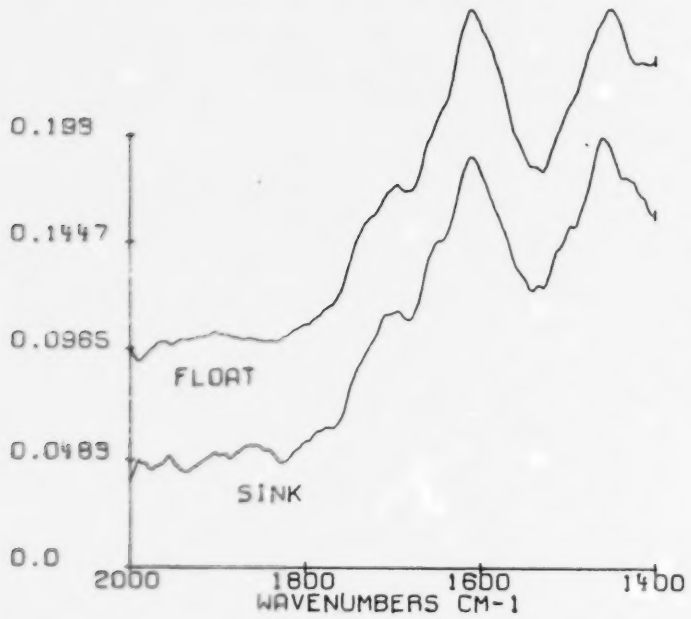


FIGURE P-651-3

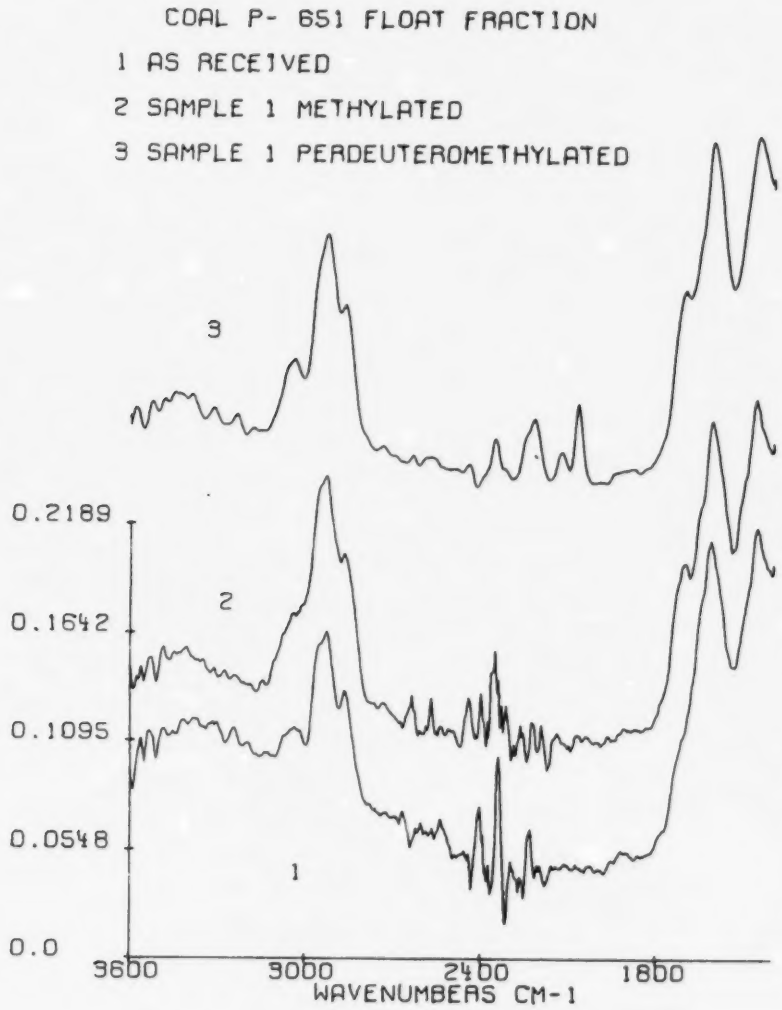


FIGURE P-651-4

COAL P-651

TOP - DEMINERALIZED "SINK" FRACTION

BOTTOM - FLOAT FRACTION @ S.G. 1.3, - 20 mesh

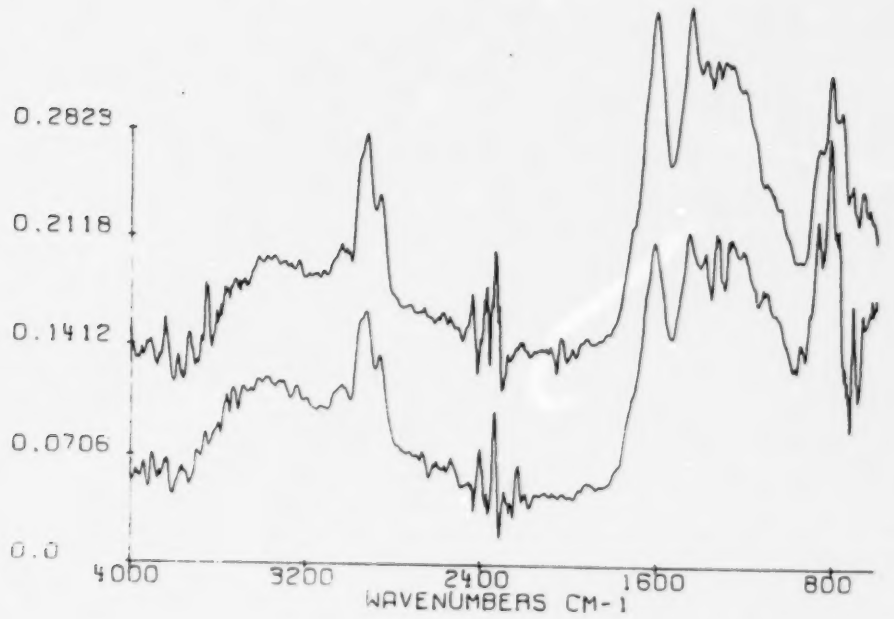


FIGURE P-651-5

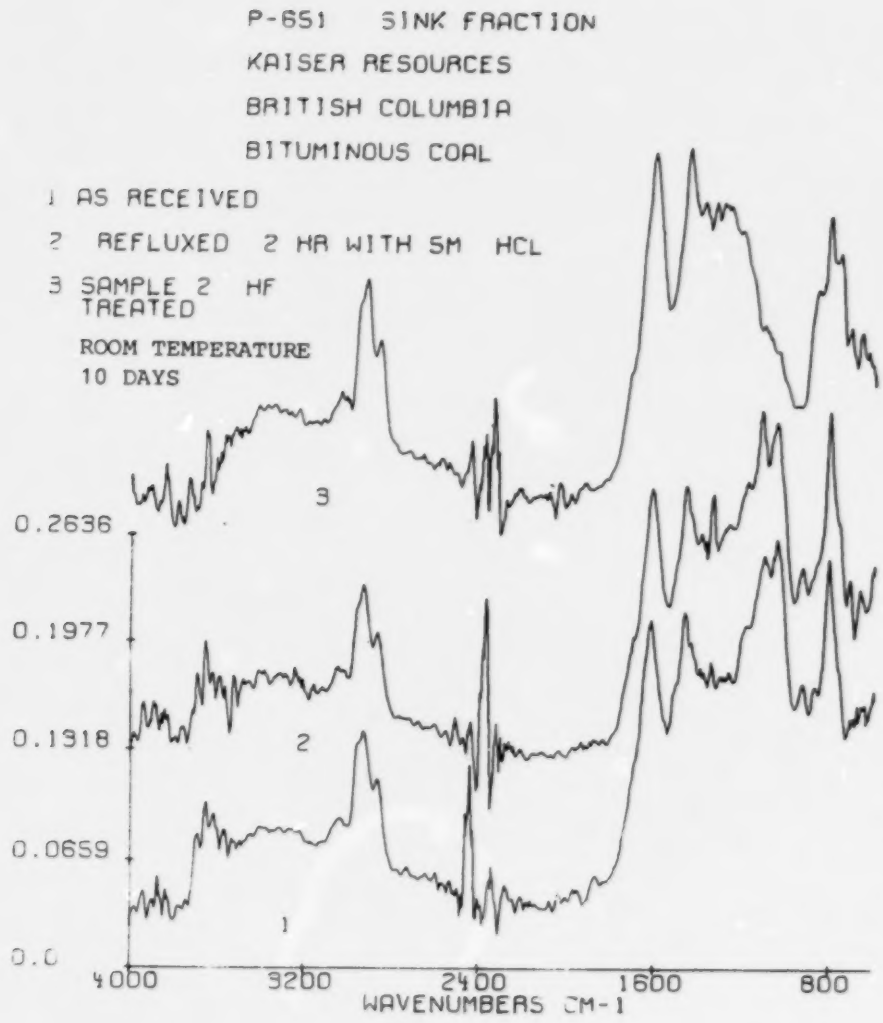


FIGURE P-651-6

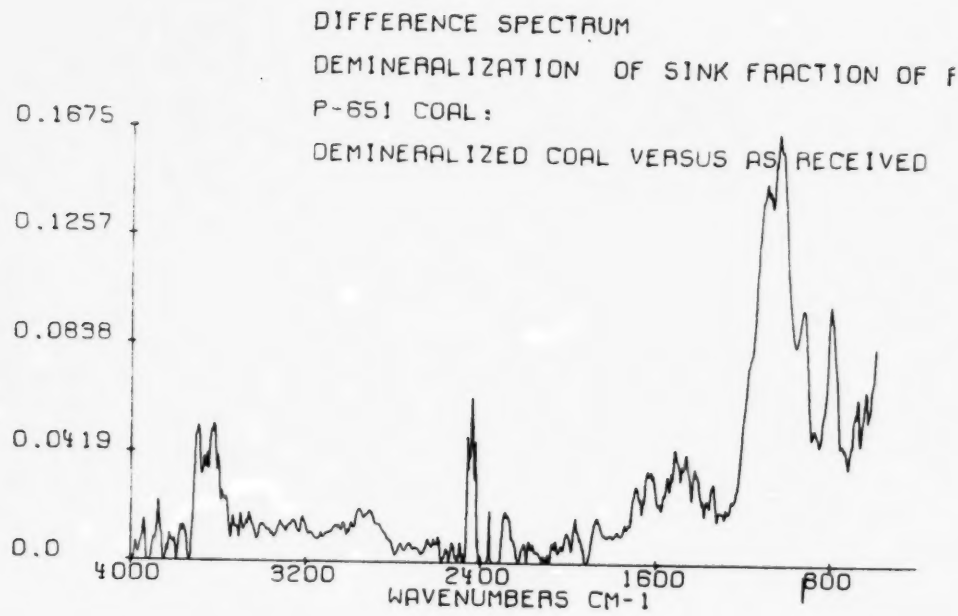


FIGURE P-651-7

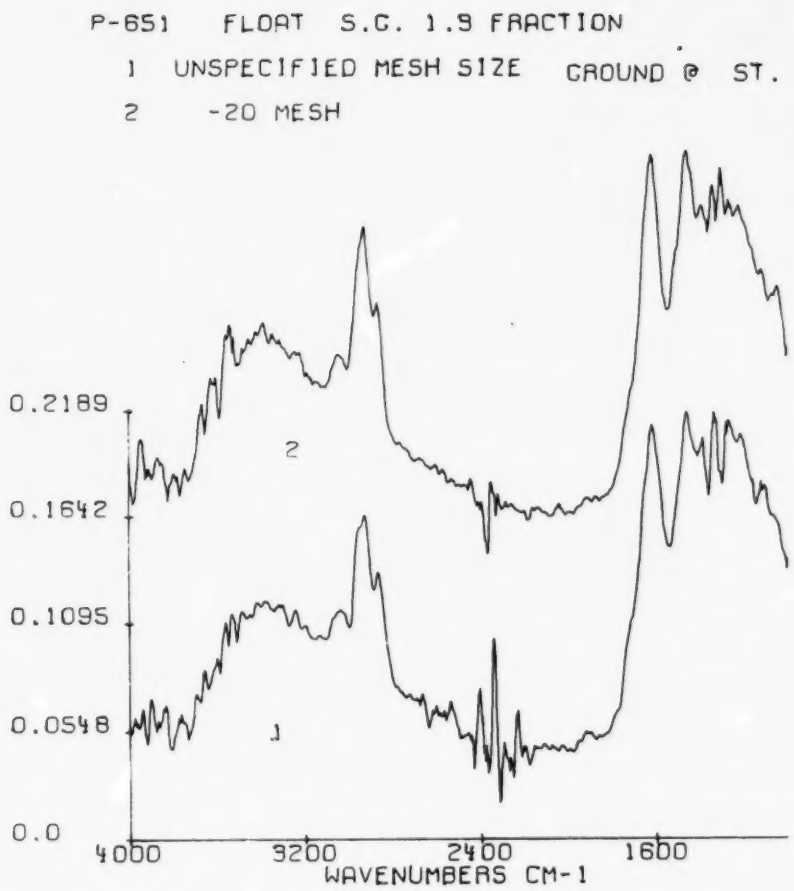


FIGURE P-651-8

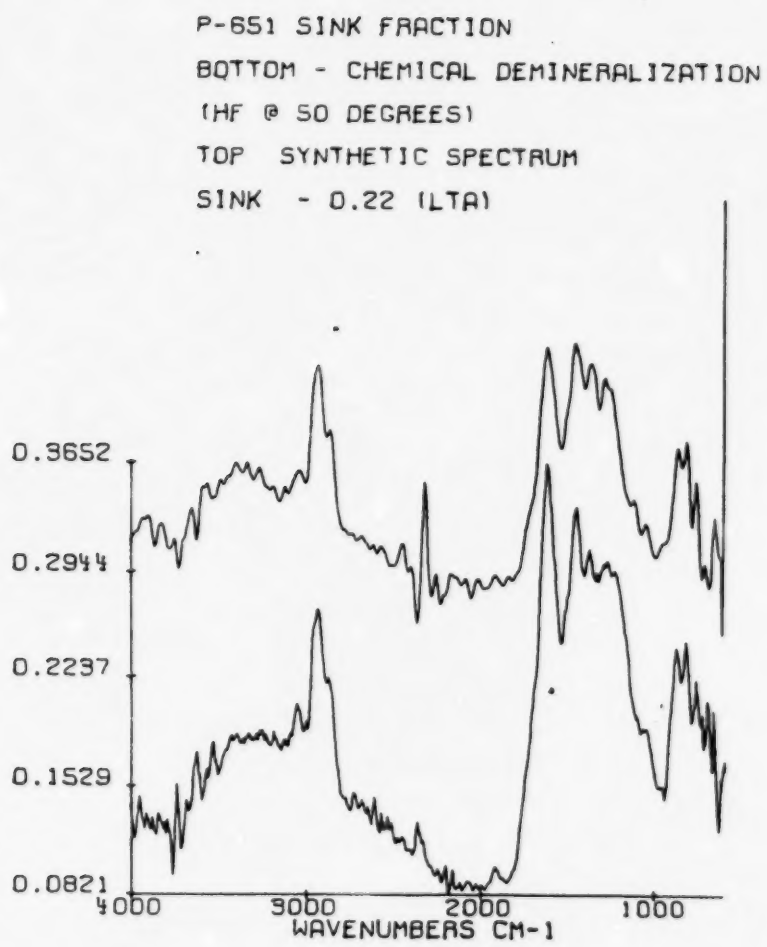


FIGURE P-651-9

COAL P-651

LOW-TEMPERATURE ASH FROM
SINK FRACTION
(PRINCIPALLY KAOLINITE)

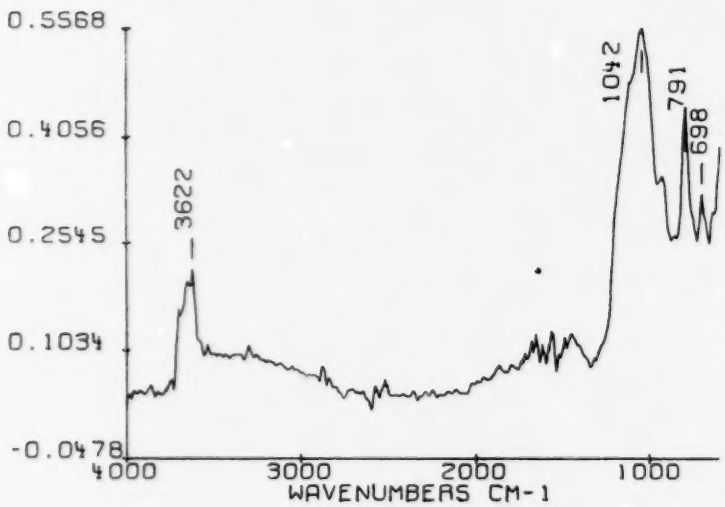


FIGURE P-651-10

MISCELLANEOUS EXAMPLES OF PAIFT SPECTRA

(A) SUB-BITUMINOUS COAL SAMPLES, COAL P-668

These samples already contain appreciable quantities of carboxylic acid functions, and the changes on oxidation are significantly less than those occurring for analogous oxidations of bituminous coals.

Figure P-668-1 illustrates this for a series oxidized for various periods, while Figure P-668-2 is a difference spectrum between the most extensively oxidized and the "as received" coal. The differences are not confined to the ketonic and carboxylic regions and indicate real differences in the relative intensities of the "1600 cm.-1 band" in these samples.

Part of the difficulty may reflect the presence of variable amounts of alkaline mineral material in these coals, and Figures P-668-3 and P-668-4 indicate that the carboxyl intensity for the sample oxidized for 7 days at 105 degrees increases markedly on treatment with mineral acid. This would have been a desirable treatment for all of this series of samples, but insufficient quantities remained after the initial spectra and some quantitative methylations. However, some spectra of other oxidized, then methylated coal samples (Figure P-668-5) show detectable changes in the ratioed carbonyl intensity after 358 hours oxidation at 120 degrees, but very significant changes occur in the 1600 cm.-1 band after 24 hours.

Figure P-668-4 also shows that "coarse" particles (approximately 20 mesh) and "fine" (approximately 200 mesh) yield approximately equivalent PAIFT spectra.

(B) GENERATION OF VICINAL ACID ANHYDRIDES BY OXIDATION OF BITUMINOUS COALS AT 300 DEGREES

In earlier discussion (p.11) it was suggested that extensively oxidized bituminous coals will probably contain appreciable proportions of ortho-sited pairs of carboxylic acid groups, and that such groups may dehydrate spontaneously to yield anhydrides of the type of phthalic anhydride.

Experimental evidence for this suggestion has been obtained.

As a typical example, oxidation of the bituminous coal sample P-649 was carried out for 30 minutes, with opportunity for escape of water vapor (by the simple device of using a wide-mouth beaker as reaction vessel).

The PAIFT spectrum (Figure P-649-1) indicates the generation of such anhydride functions (antisymmetric vibration, 1843 cm.-1, symmetric vibration, 1773 cm.-1). The formation of the anhydrides is critically dependent upon the loss of water vapor from the reactor.

Figure P-649-2 indicates that restriction of the air flow over the sample (by using a narrow-mouth conical flask as reactor) eliminates the anhydride generation.

Figure P-649-3 is a difference spectrum of the two above, enhancing the visibility of the anhydride carbonyl stretching features, and

Figure P-649-4 is a full presentation of the partial spectra in Figures P-649-1 and P-649-2.

Extensively oxidized coals of this type have lost almost all their aliphatic C-H functionality, but still retain sufficient bonds linking aromatic rings to lack solubility. They would be interesting candidate substances for attempted characterization by other techniques.

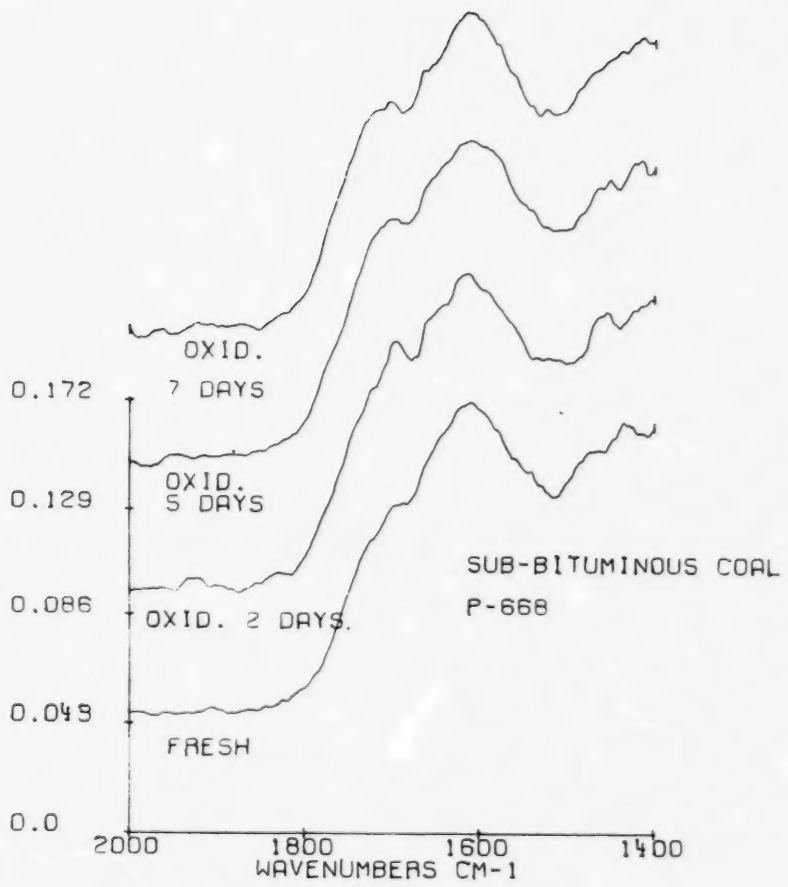


FIGURE P-668-1

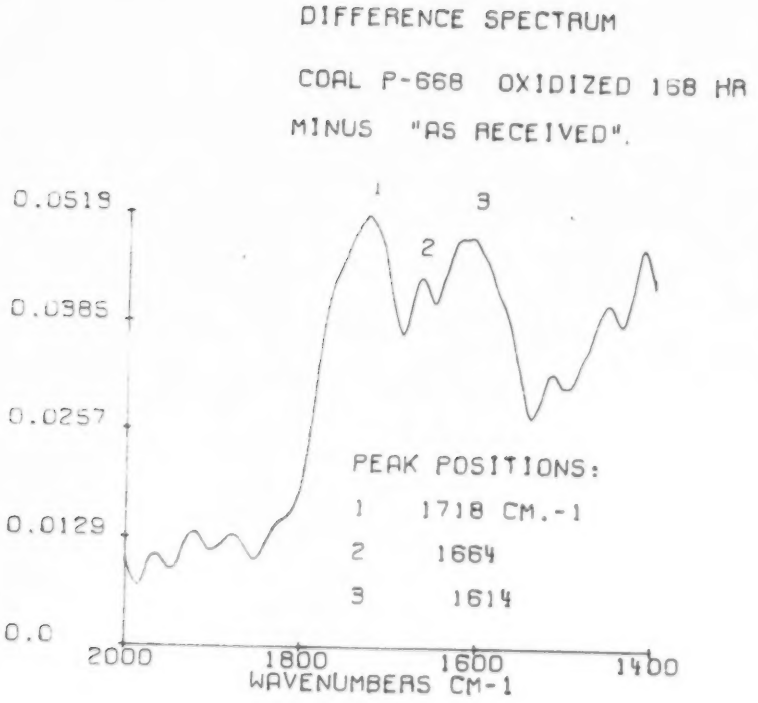


FIGURE P-668-2

COAL P-668

TOP OXIDIZED 168 HR @ 105 DEC.

BOTTOM AS RECEIVED

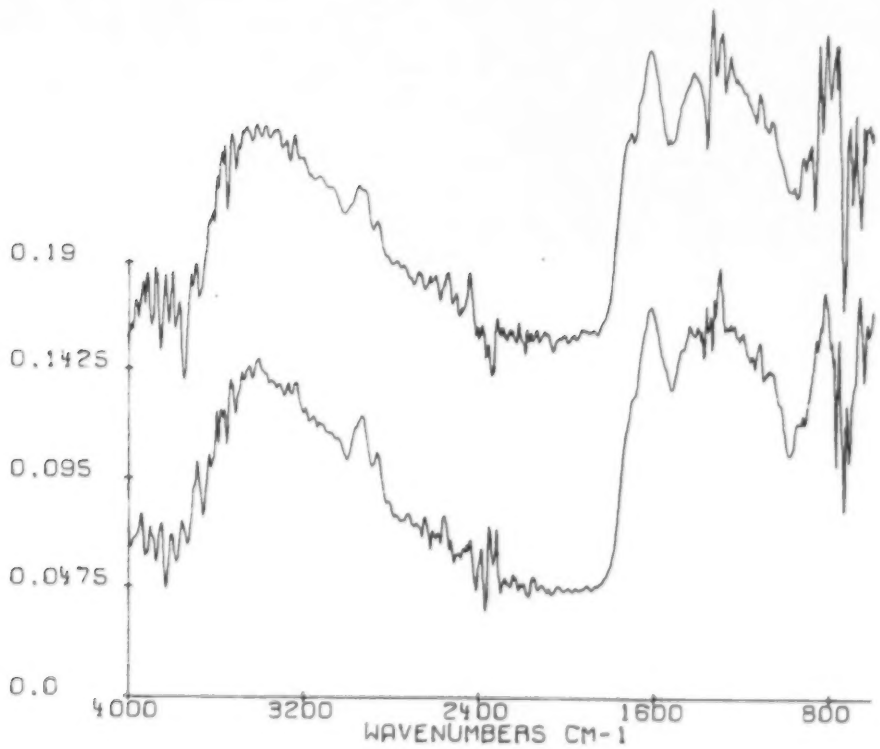


FIGURE P-668-3

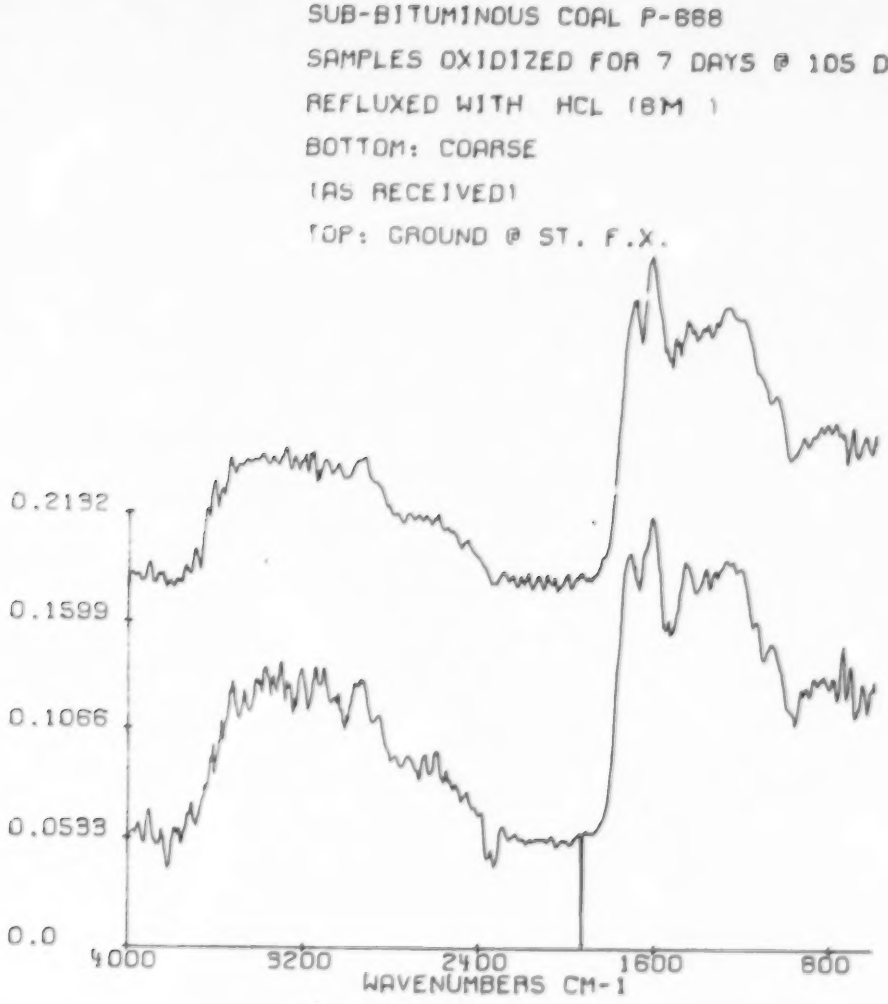


FIGURE P-668-4

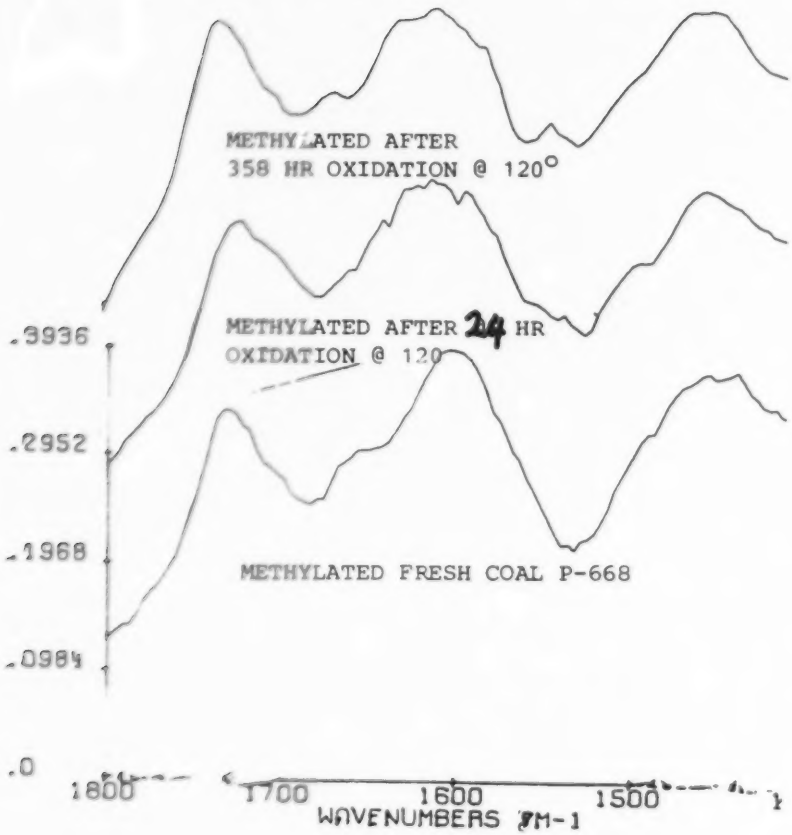


FIGURE P-668-5

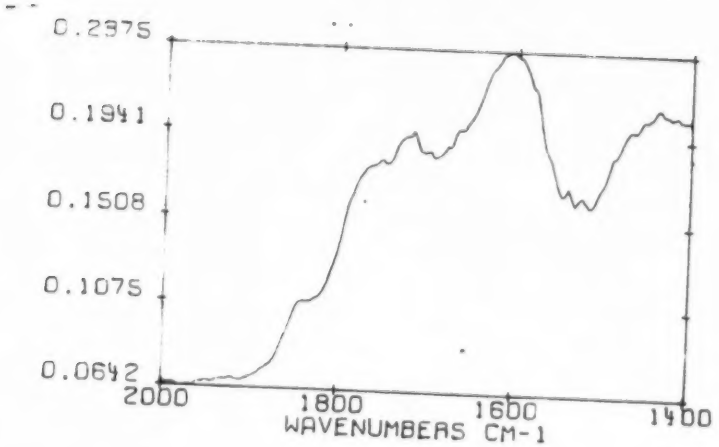


FIGURE P-649-1

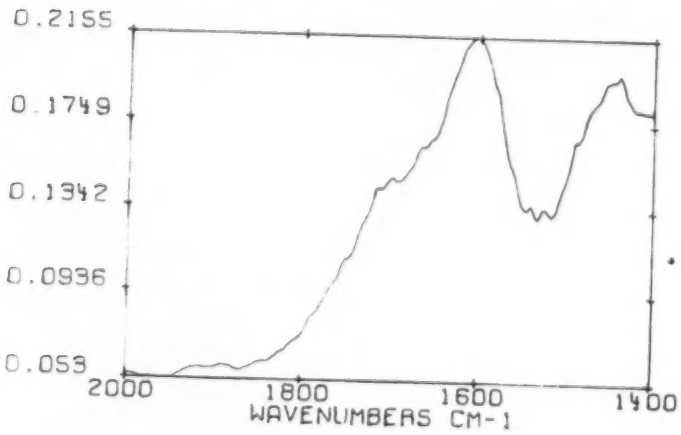


FIGURE P-649-2

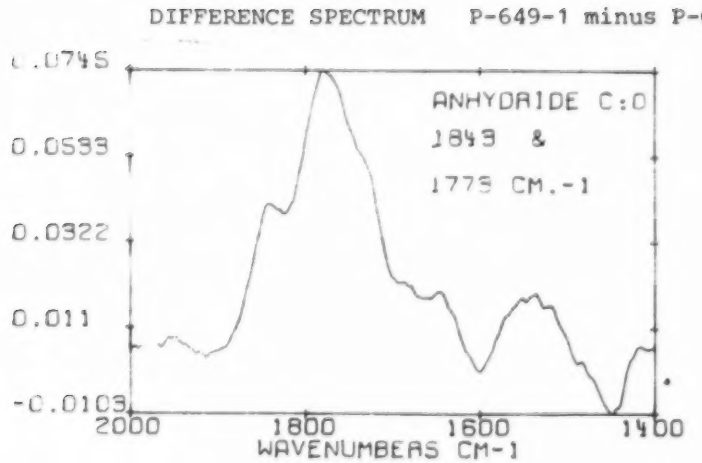


FIGURE P-649-3

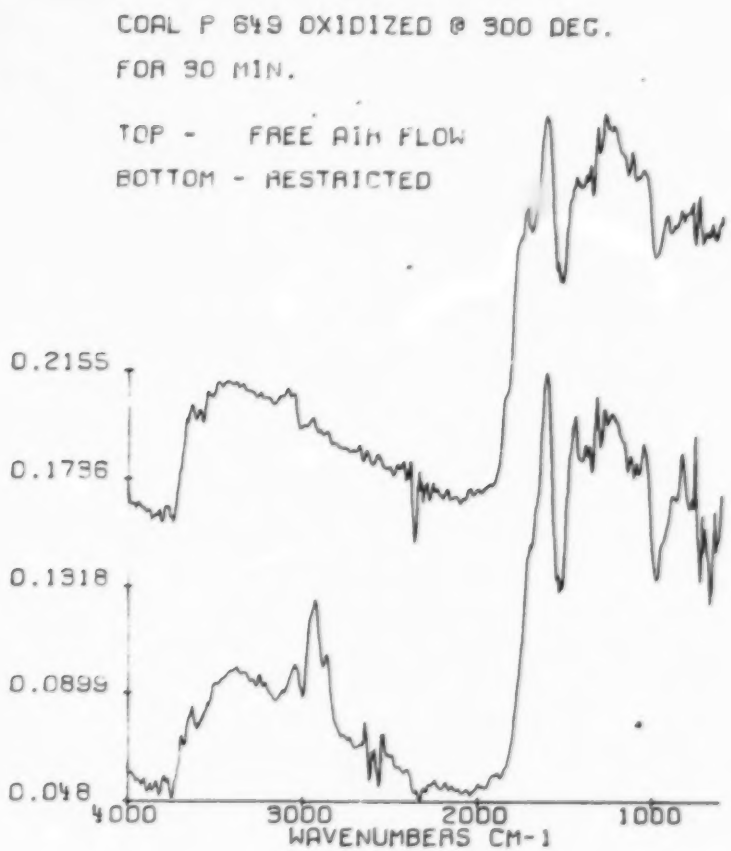


FIGURE P-649-4

CONCLUSIONS

It is evident from the cited results in this report that photoacoustic infrared Fourier Transform (PAIFT) spectroscopy has the capability to provide a rapid and sensitive indication of the extent of coal oxidation, and of the changes occurring on semicoke formation, and of the differences among partially fractionated coals. Routine or service measurements seem practical although the sensitivity of detection of low levels of oxidation (below those evident from any other spectroscopic accessory technique) leads to the conclusion that there was no truly "fresh" coal (i.e. almost free of carbonyl functionality) among the samples provided for this study.

The success of the particular configuration of basic FTIR system and photoacoustic accessory system, which provides a sensitive, rapid, and experimentally straightforward technique yielding optimal results, should not be taken as a blanket recommendation for the interfacing of the present photoacoustic detector to other types of FTIR spectrometer. The Bruker IFS110 possesses a particularly quiet, precise, interferometer drive, and a relatively large throughput light intensity.

ACKNOWLEDGEMENTS

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